

UV-Visible: Spectroscopy Focus

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Spectroscopic Needs for Atmospheric Remote-Sensing, San Diego, October 22-26, 2001

About the UV-visible

- **very large user community**
 - ... Dobson, Brewer, ...
 - ... surface ozone (photometers)
 - ... DOAS ...
 - ... satellites (TOMS, GOME, OMI, MAESTRO ...)
- **radiative transfer models**
 - ... multiple scattering
 - ... spherical geometry
 - ... polarisation

General Questions (1):

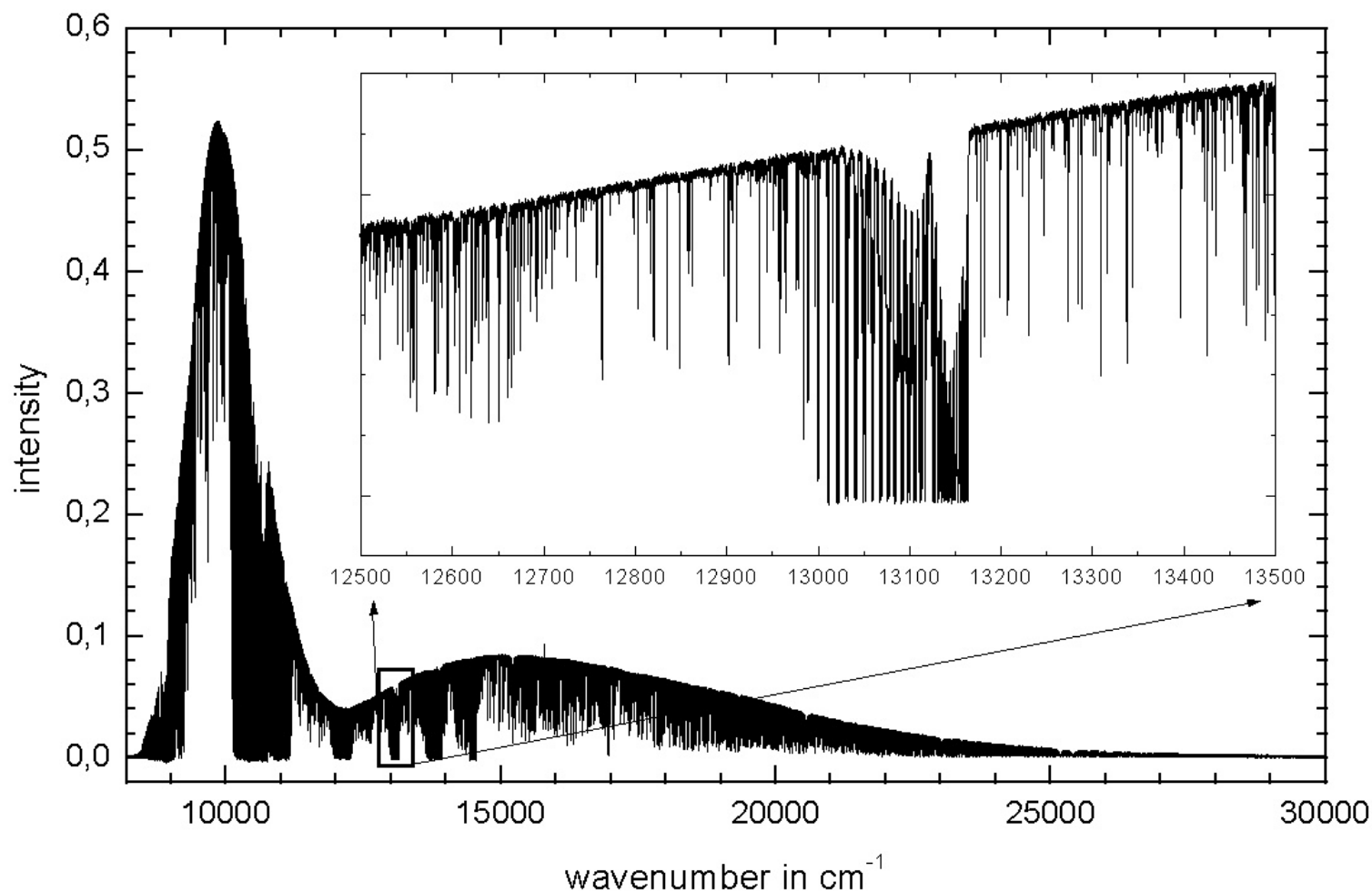
- Which molecules need to be studied ?
- What are the requirements for the „users“ ?
 - ... spectral range
 - ... spectral resolution
 - ... temperature range
 - ... signal/noise ratio
 - ... pressure effects
 - ... uncertainties

General Questions (2):

- What are the limits (e.g. 1% for intensities) ?
- Can we model the laboratory spectra ?
- Who compares different laboratory data ?
- Is laboratory work supported sufficiently ?
- Is quantitative spectroscopy interesting ?
 - ... for students
 - ... for our colleagues
 - ... for the funding agencies

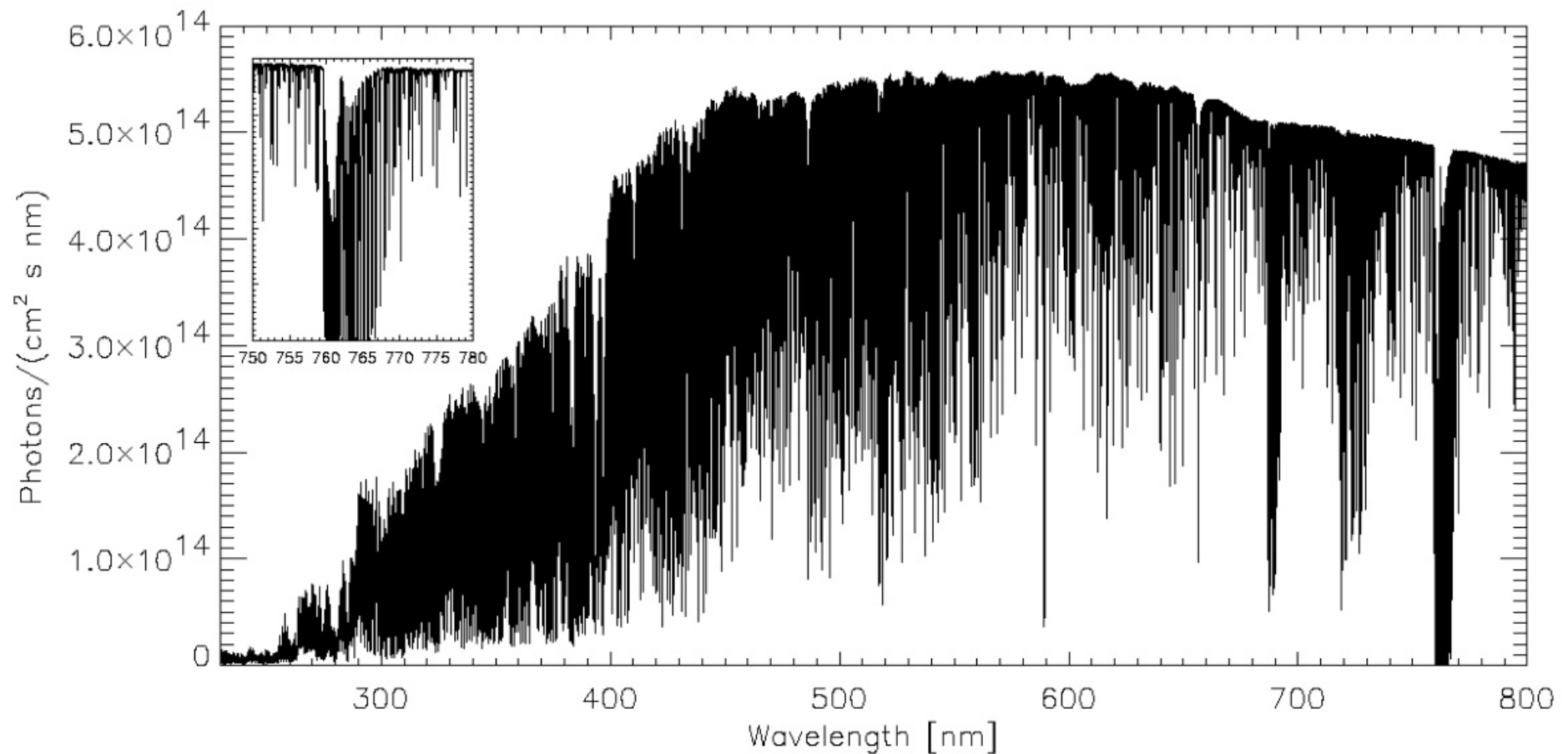
Introduction: The complexity of the task

Ground-based solar-occultation spectrum (FTS):



Introduction: The complexity of the task

The one and only high-resolution sun reference:

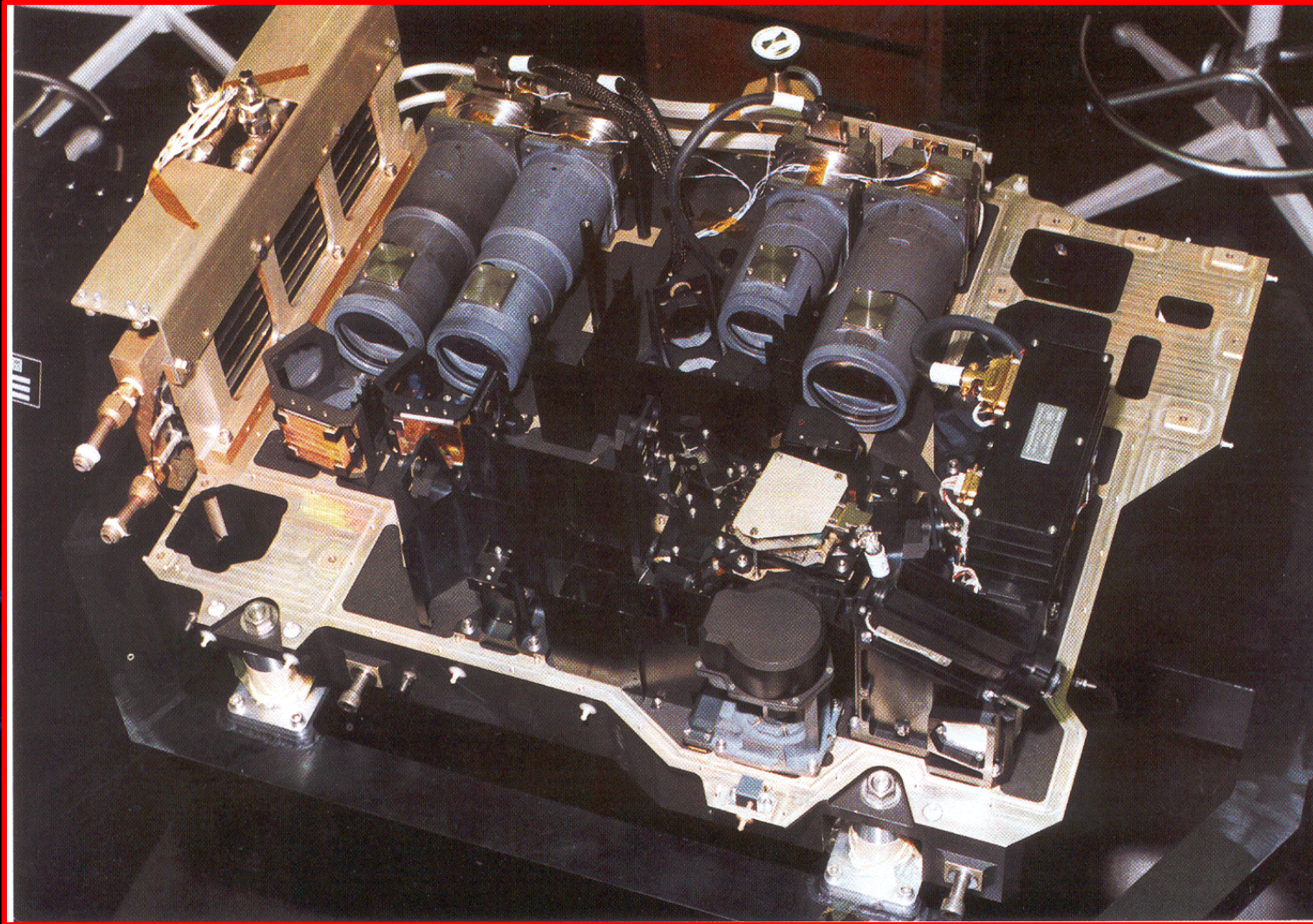


Source: Kurucz et al., courtesy of T. Kurosu (SAO Harvard)

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Introduction: New satellite instruments

GOME-FM in 1994:

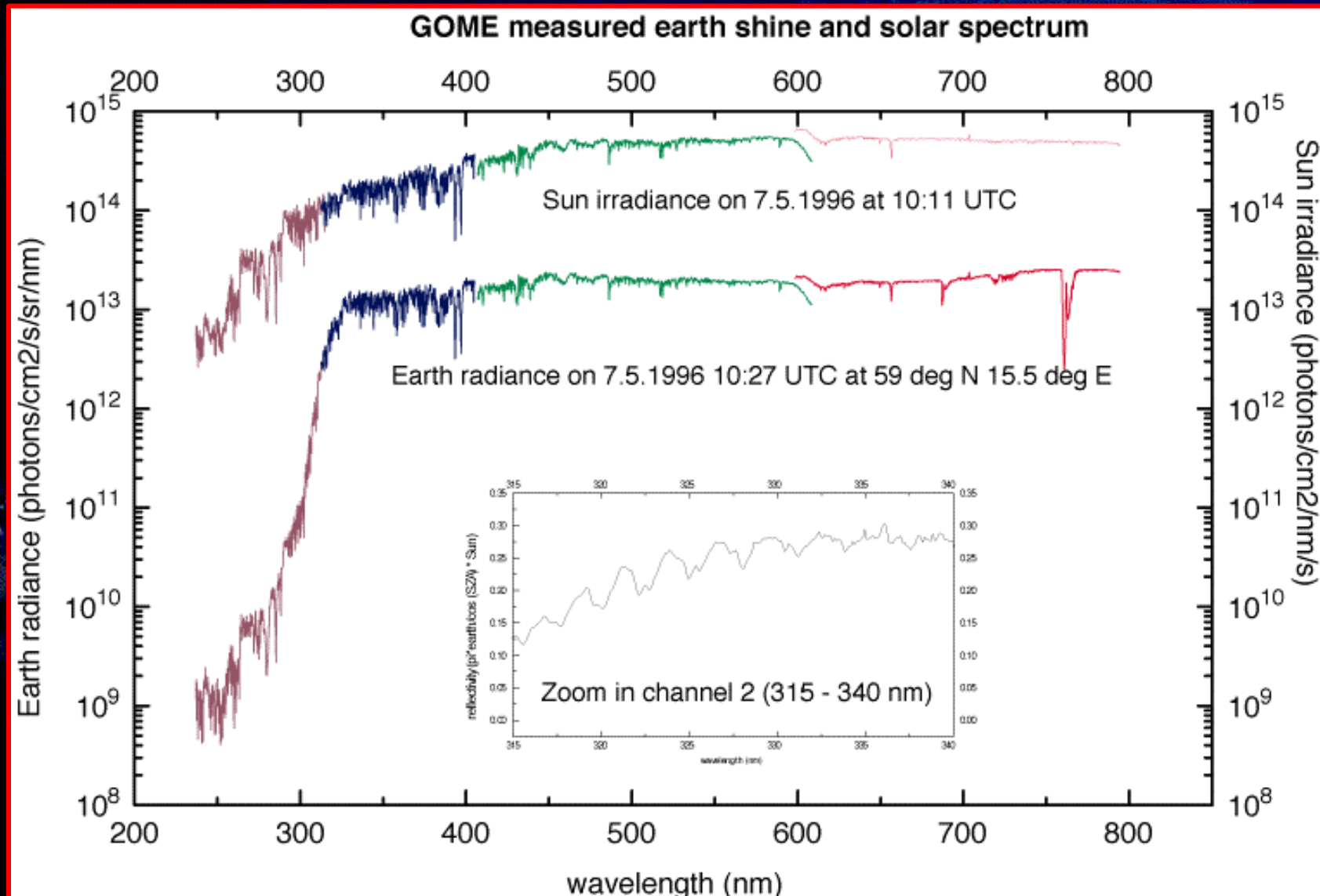


Source: The GOME Users Manual, ESA-ESTEC, 1995

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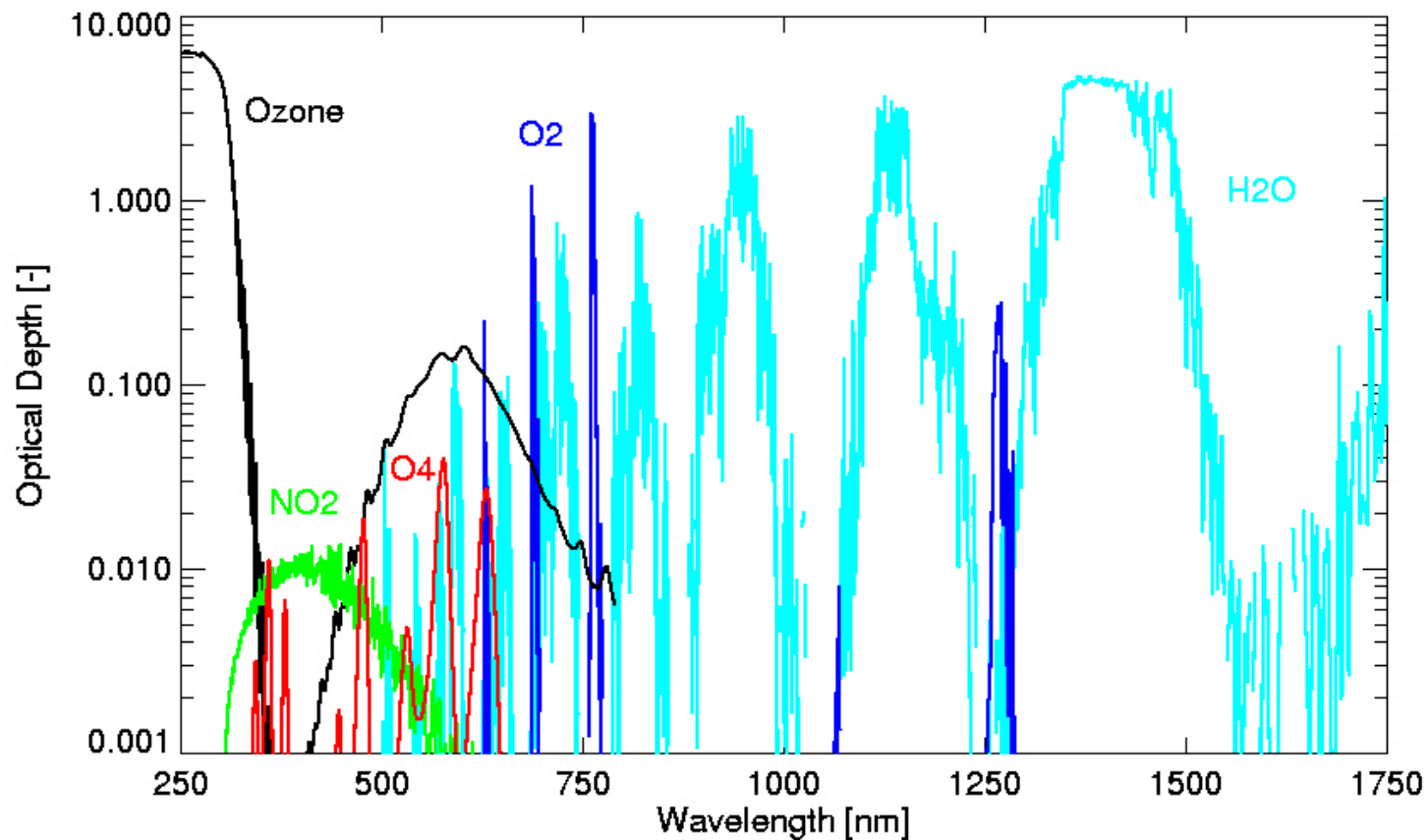
Introduction: New satellite instruments

The GOME spectra (1995-2001):



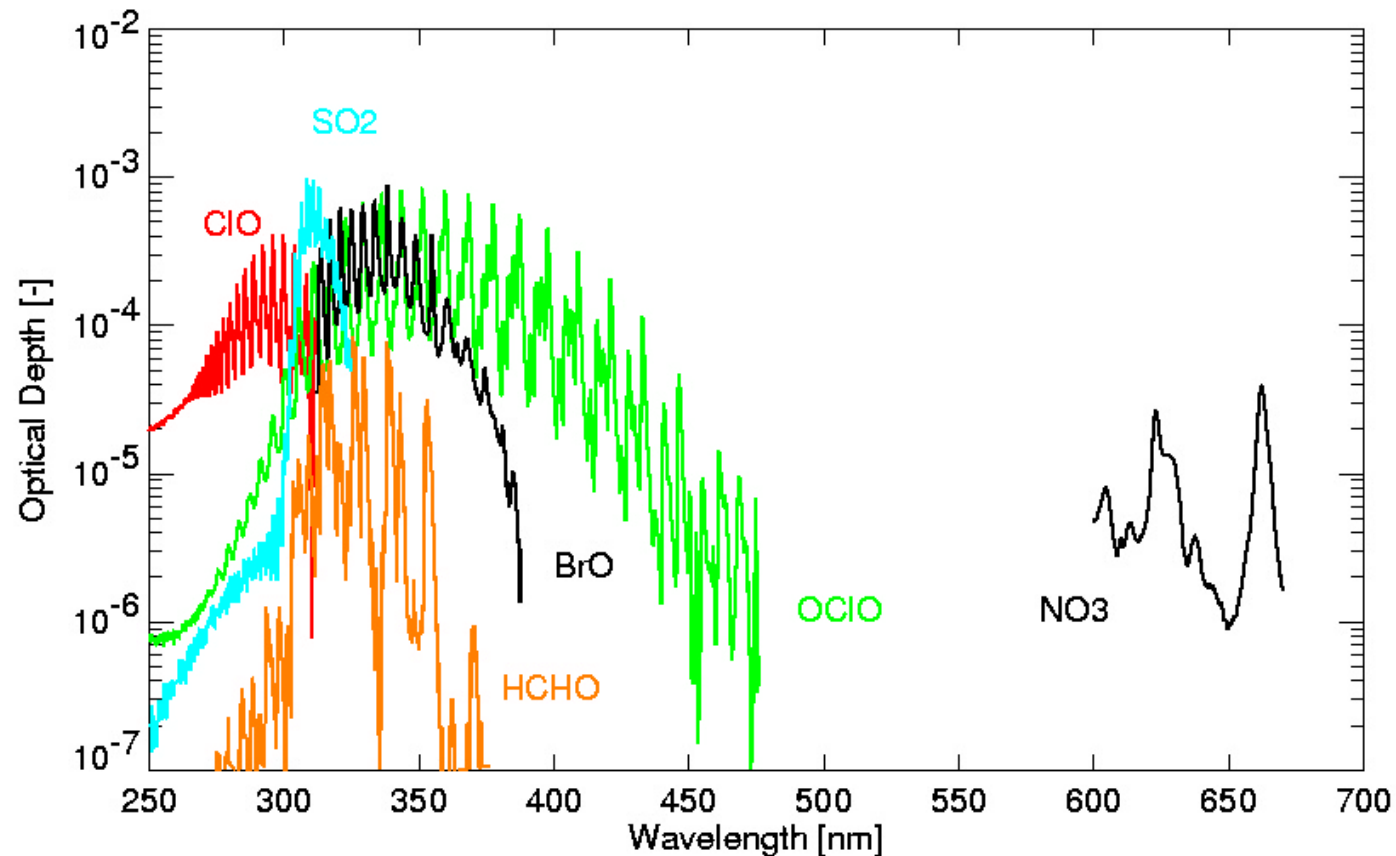
Introduction: New satellite instruments

Atmospheric trace gases (1):



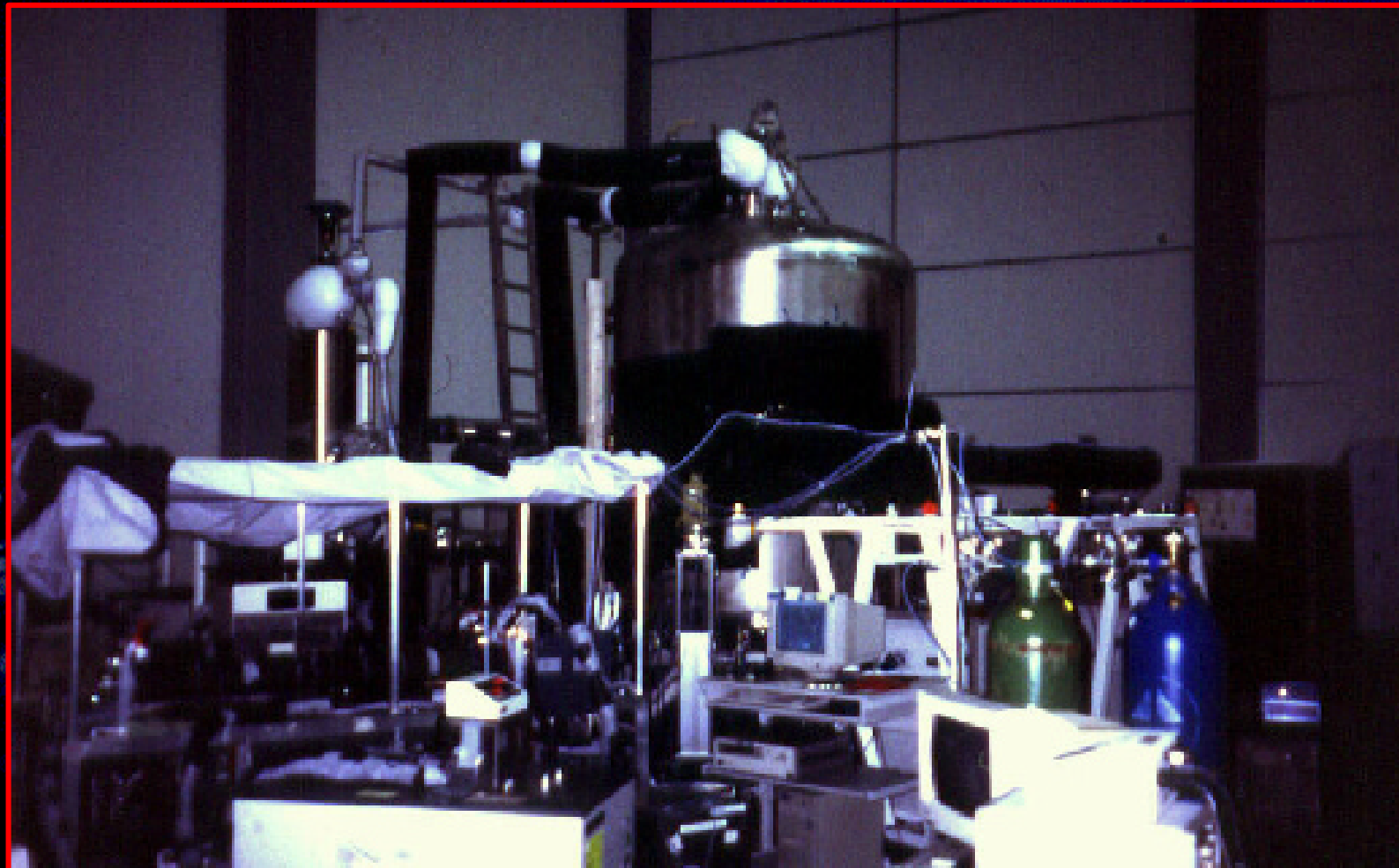
Introduction: New satellite instruments

Atmospheric trace gases (2):



Introduction: New satellite instruments

New reference data have been recorded (1):



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Introduction: New satellite instruments

New reference data have been recorded (2):



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A few observations:

- **diode-array spectra have very high signal/noise**
 - ... but often poor wavelength accuracy
 - ... and only low or medium spectral resolution
- **FTS has very high wavelength accuracy**
 - ... and very high spectral resolution
 - ... but often only medium signal/noise
- **there are very weak features (O_2 , H_2O , ...)**
 - ... but new techniques are available (CRD)
- **many different reference spectra are used**

Available O₃ and NO₂ data have been compared:

A Critical Review of the Absorption Cross-Sections of O₃ and NO₂ in the 240–790 nm Region

Part 1. Ozone

DRAFT VERSION

March 29, 2001

Prepared by

Johannes Orphal,
Chargé de Recherche (CNRS, Orsay, France)

for the

European Space Agency (ESA-ESTEC, Noordwijk, The Netherlands)
Earth Science Division

A Critical Review of the Absorption Cross-Sections of O₃ and NO₂ in the 240–790 nm Region

Part 2. Nitrogen Dioxide

DRAFT VERSION

July 20, 2001

Prepared by

Johannes Orphal,
Chargé de Recherche (CNRS, Orsay, France)

for the

European Space Agency (ESA-ESTEC, Noordwijk, The Netherlands)
Earth Science Division

J. Orphal, ESA Special Publication, in press (2001)

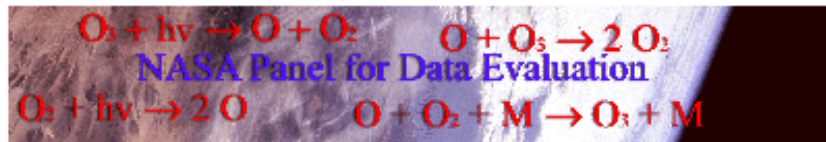
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... and there are evaluations for photochemistry:



IUPAC Subcommittee for Gas Kinetic Data Evaluation
International Union of Pure and Applied Chemistry (IUPAC)

<http://www.iupac-kinetic.ch.cam.ac.uk/>



*Chemical Kinetics and Photochemical
Data for Stratospheric Modeling -- Evaluation 13*
Supplement to Evaluation 12: Update of Key Reactions
JPL Publication No. 00-3

<http://jpldataeval.jpl.nasa.gov/>

Case 1: Oxygen O₂ A band

Precise Line Parameters and Transition Probability of the Atmospheric A Band of Molecular Oxygen ¹⁶O₂, R. Schermaul and R. C. M. Learner, *J. Quant. Spectrosc. Radiat. Transfer* **61**, 781-794, 1999.

Transition Probability and Line Broadening for the $b^1S_g^+$ ($\nu=0$) - $X^3S_g^-$ ($\nu=0$) Band of the ¹⁶O¹⁸O Isotopomer of Oxygen, R. Schermaul, *J. Quant. Spectrosc. Radiat. Transfer* **62**, 181-191, 1999.

Experimental Line Parameters of the Oxygen A Band at 760 nm, L. R. Brown and C. Plymate, *J. Molec. Spectrosc.* **199**, 166-179, 2000.

Molecular Constants for the $\nu = 0$, $b^1S_g^+$ Excited State of O₂: Improved Values Derived from Measurements of the Oxygen A-Band Using Intracavity Laser Spectroscopy, L. C. O'Brien, H. Cao, and J. J. O'Brien, *J. Molec. Spectrosc.* **207**, 99-103, 2001.

Who compares and recommends data?

Case 2: Oxygen O₂ in the UV (1)

Correction of the oxygen interference with UV spectroscopic (DOAS) measurements of monocyclic aromatic hydro-carbons in the atmosphere, R. Volkamer, T. Etzkorn, A. Geyer, and U. Platt, *Atmos. Environ.* **32**, 3731-3747, 1999.

The Wulf bands of Oxygen, P. Bernath, M. Carleer, S. Fally, A. Jenouvrier, A. C. Vandaele, C. Hermans, M.-F. Mérienne, and R. Colin, *Chem. Phys. Lett.* **297** (3-4), 293-299, 1998.

Fourier transform spectroscopy and cross-section measurements of the Herzberg III bands of O₂ at 295 K, K. Yoshino, J. R. Esmond, W. H. Parkinson, A. P. Thorne, R. C. M. Learner, G. Cox, and A. S.-C. Cheung, *J. Chem. Phys.* **112**, 9791-9801 (2000).

Fourier transform spectroscopy and cross-section measurements of the Herzberg II bands of O₂ at 295 K, K. Yoshino et al., *J. Chem. Phys.* **111**, 2960-2967 (1999).

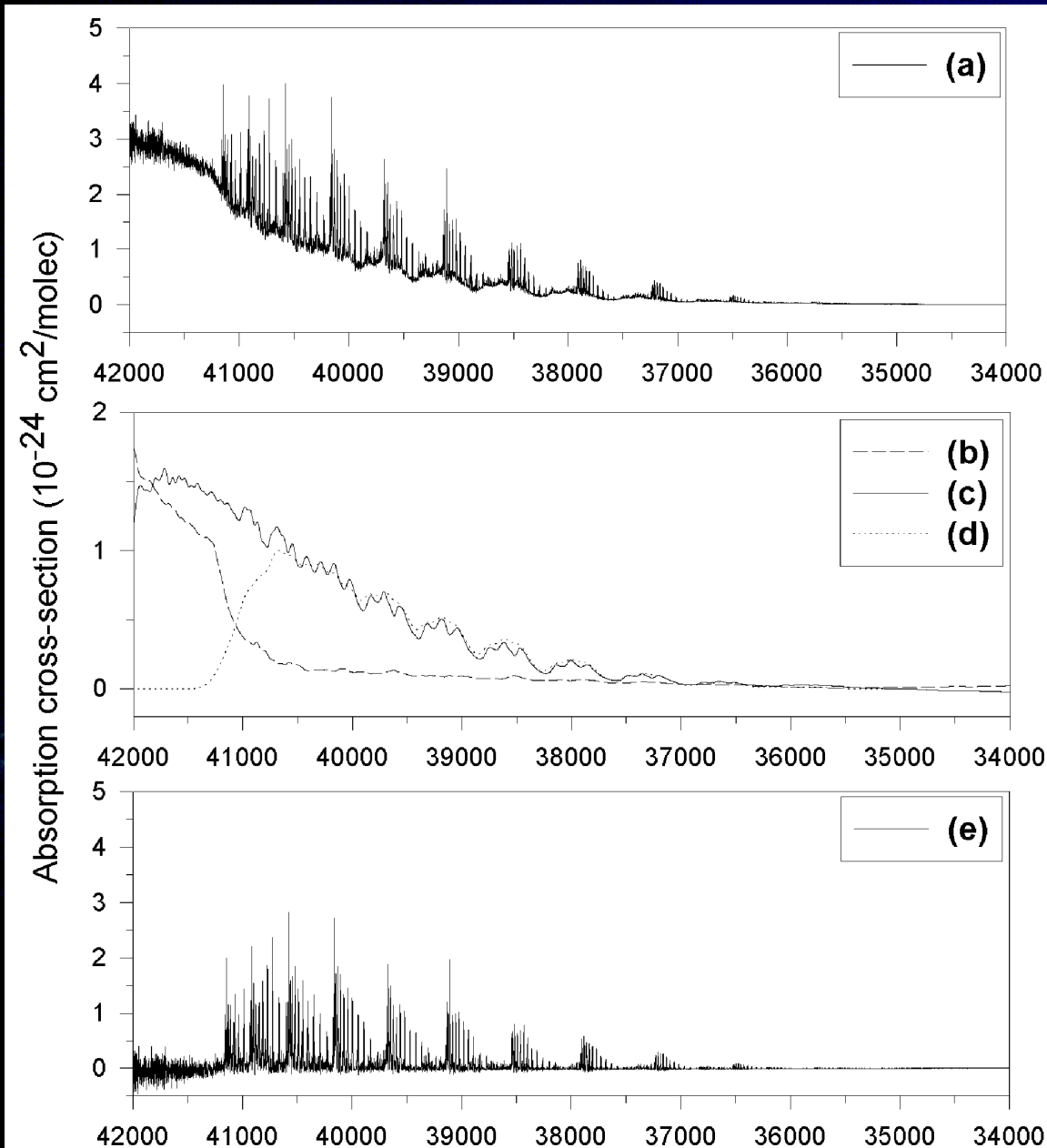
Case 2: Oxygen O₂ in the UV (2)

Fourier transform spectroscopy of the O₂ Herzberg bands. III. Absorption cross-sections of the collision-induced bands and of the Herzberg continuum, S. Fally S., A. C. Vandaele, M. Carleer, C. Hermans, A. Jenouvrier M.-F. Mérienne, B. Coquart, and R. Colin, *J. Mol. Spectrosc.* **204**, in press (2001).

Fourier transform spectroscopy of the O₂ Herzberg bands. II. Band oscillator strengths and transition moments, M.-F. Mérienne, A. Jenouvrier, B. Coquart, M. Carleer, S. Fally, R. Colin, A. C. Vandaele, and C. Hermans, *J. Mol. Spectrosc.* **202**(2), 171-193 (2000).

Fourier transform spectroscopy of the O₂ Herzberg bands. I. Rotational analysis, A. Jenouvrier, M.-F. Mérienne, B. Coquart, M. Carleer, S. Fally, A. C. Vandaele, C. Hermans, and R. Colin, *J. Mol. Spectrosc.* **198**, 36-162 (1999).

Case 2: Oxygen O₂ in the UV (3)



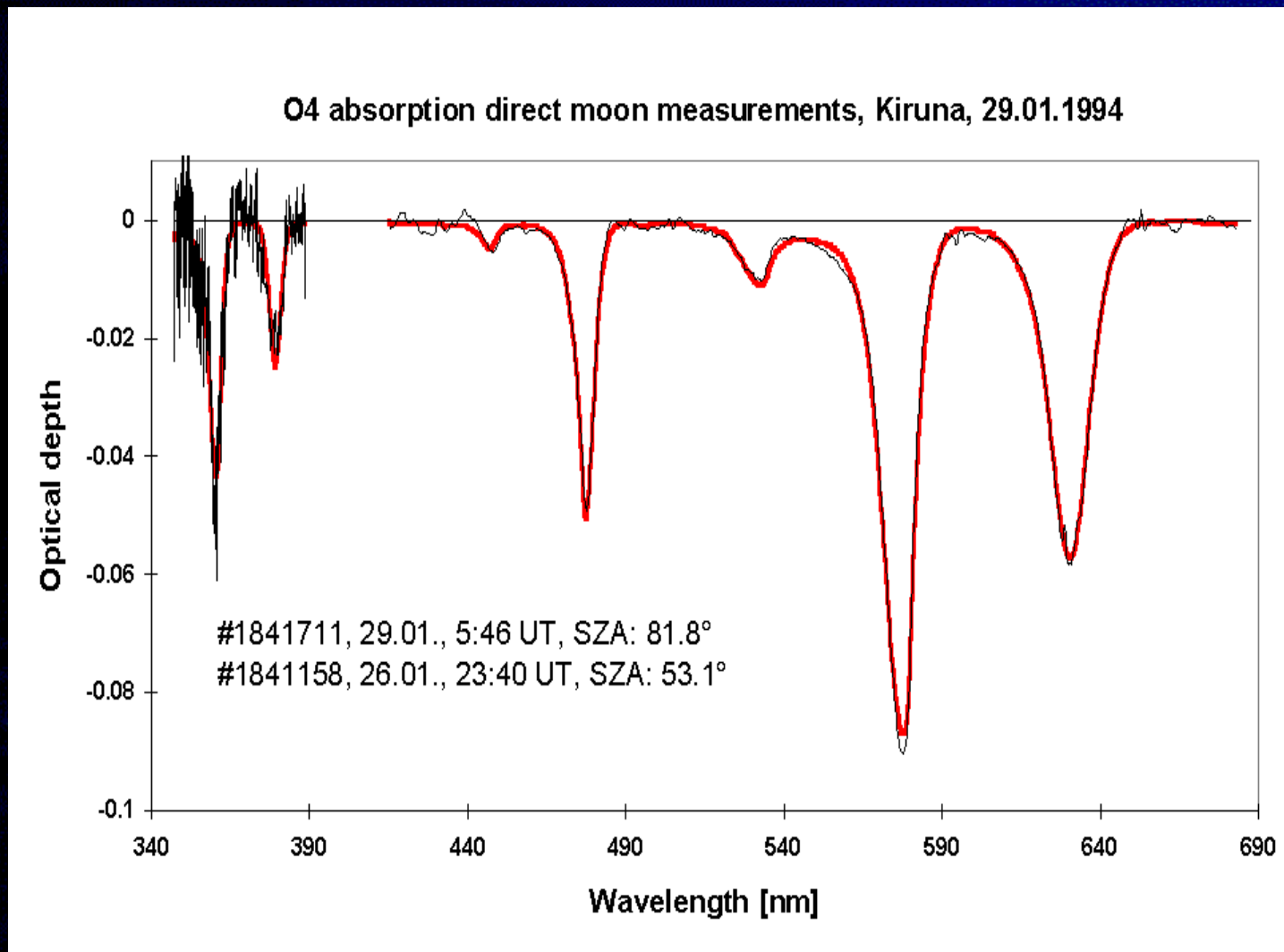
There are:

- Herzberg bands
- Wulf bands (CIA)
- Schumann-Runge

„Users“ have some difficulties to use the available data.

Is it in HITRAN?

Case 3: The oxygen „dimer“ (O₂)₂ (1)



Source: T. Wagner, C. von Friedeburg, O. Klimm, C. Otten, and U. Platt, UV/vis observations of atmospheric O₄ absorptions using direct moon light and zenith scattered sunlight under clear and cloudy sky conditions, paper in preparation. (2001)

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Case 3: The oxygen „dimer“ (O₂)₂ (2)

Absorption measurements of oxygen between 330 and 1140 nm, Greenblatt G. D., J.J. Orlando, J.B. Burkholder, and A.R. Ravishankara, *J. Geophys. Res.* **95**, 18577-18582, 1990.

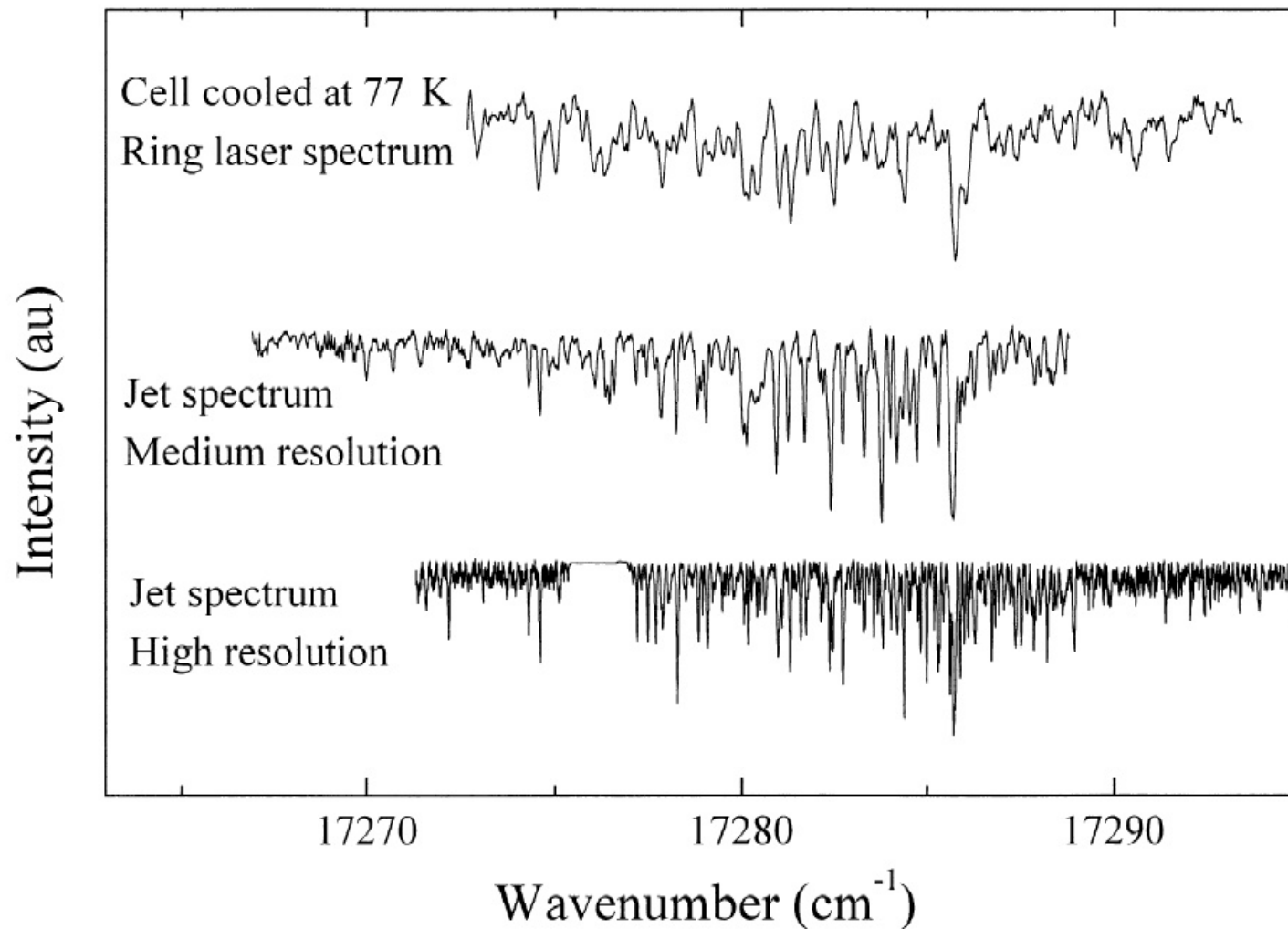
Visible absorption cross section and integrated absorption intensities of molecular oxygen (O₂ and O₄), D. A. Newnham and J. Ballard, *J. Geophys. Res.* **103**, 28801-28816, 1998.

Visible absorption bands of the (O₂)₂-collision complex at pressures below 760 Torr, H. Naus and W. Ubachs, *Appl. Optics* **38**, 3423-3428, 1999.

Rotationally resolved absorption spectrum of the O₂ dimer in the visible range; A. Campargue, L. Bienneir, R. Jost, B. Bussety-Honvault, V. Veyret, S. Churassy, and R. Bacis, *Chem. Phys. Lett.* **288**, 734, 1998.

Case 3: The oxygen „dimer“ (O₂)₂ (3)

A. Campargue et al. / Chemical Physics Letters 288 (1998) 734–742



Can we model the laboratory data?

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Case 4: Water H₂O (1)

The contribution of unknown weak water vapour lines to the absorption of solar radiation, R. C. M. Learner et al., *Geophys. Res. Lett.* **26**, 3609-3612, 1999.

New studies of the visible and near-infrared absorption by water vapour and some problems with the HITRAN database, D. Belmiloud et al., *Geophys. Res. Lett.* **27**, 3703-3706, 2000.

Effects of improvements in near-infrared water vapour line intensities on short-wave atmospheric absorption, J. Chagas et al., *Geophys. Res. Letters* **28**, 2401-2404, 2001.

High-resolution atmospheric absorption by water vapour in the 830-985 nm region: Evaluation of spectroscopic databases, K. Smith and D. A. Newnham, *Geophys. Res. Lett.*, in press, 2001.

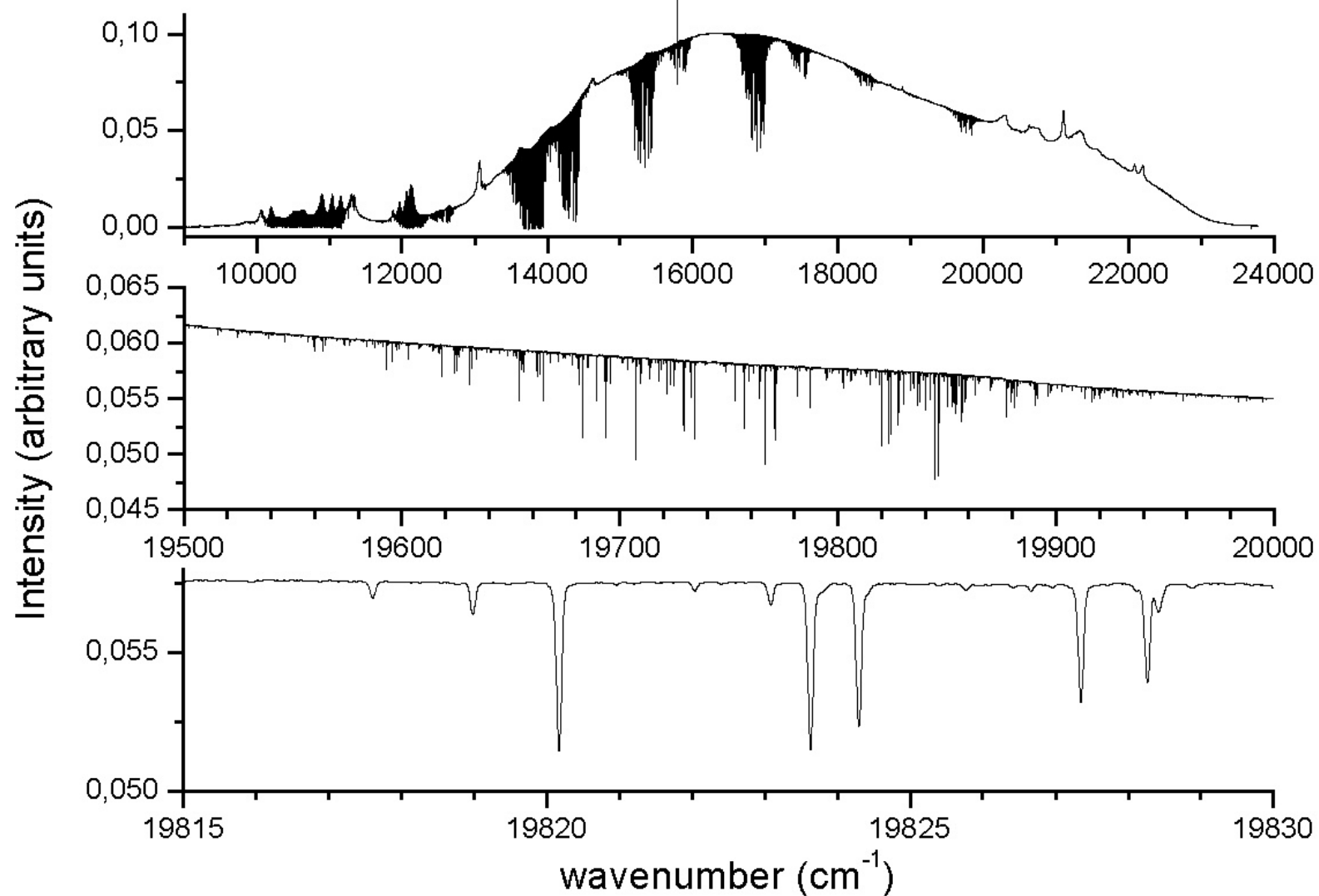
Case 4: Water H₂O (2)

The near infrared, visible and near ultraviolet overtone spectrum of water, M. Carleer, A. Jenouvrier, A.-C. Vandaele, P.F. Bernath, M.F. Mérienne, R. Colin, N.F. Zobov, O. L. Polyansky, J. Tennyson, and A. V. Savin, *J. Chem. Phys.* **111**, No2444-2450, 1999.

The near ultraviolet rotation-vibration spectrum of water, N. F. Zobov, D. Belmiloud, O. L. Polyansky, J. Tennyson, S. V. Shirin, M. Carleer, A. Jenouvrier, A.-C. Vandaele, P. F. Bernath, M. F. Mérienne, and R. Colin,, **113**, No. 4 , 1546-1551, 2000.

Cavity Ring-Down spectroscopy on water vapour in the range 555-604 nm, H. Naus, W. Ubachs, P.F. Levelt, O.L. Polyansky, N.F. Zobov, J. Tennyson, *J. Mol. Spectrosc.* **205** 117-121, 2001.

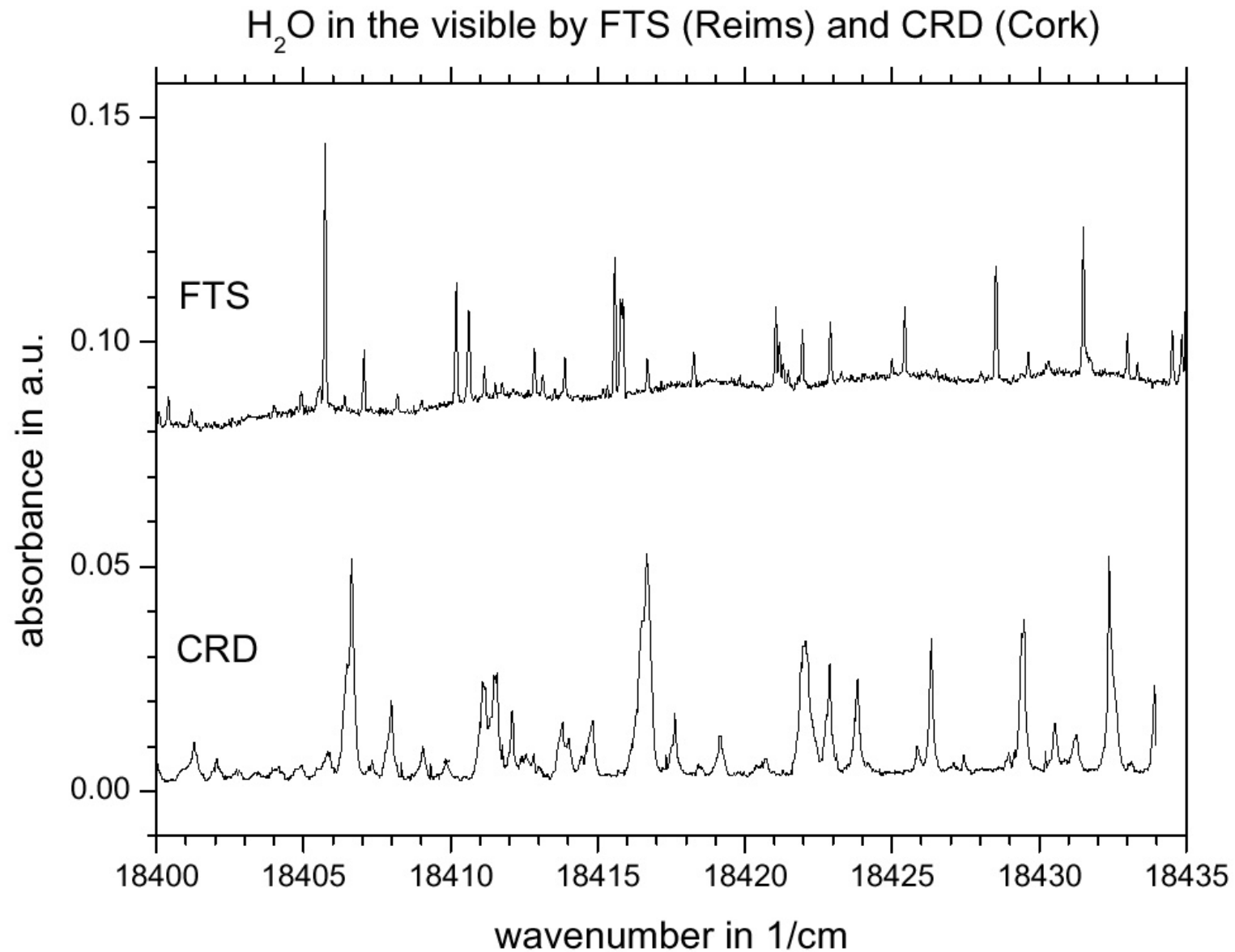
Case 4: Water H₂O (3)



Source: M. Carleer et al., personal communication, 1998.

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Case 4: Water H₂O (4)



Case 4: Water H₂O (5)

The $4\nu_{\text{OH}}$ absorption spectrum of HDO, Naumenko, E. Bertseva and A. Campargue, *J. Mol. Spectrosc.* **197**, 122-132, 1999.

The HDO absorption spectrum in the 13165-13500 cm⁻¹ spectral region. Naumenko, E. Bertseva, A. Campargue and D. Schwenke, *J. Mol. Spectrosc.* **201**, 297-309, 2000.

Comment on “The near infrared, visible, and near ultraviolet overtone spectrum of water” [*J. Chem. Phys.*, **111**, 2444, 1999], A. Campargue, E. Bertseva, and O. Naumenko, *J. Chem. Phys.* **112**, 8730-8730, 2000.

The $5\nu_{\text{OH}}$ overtone transition of HDO, E. Bertseva, O. Naumenko, and A. Campargue, *J. Mol. Spectrosc.* **203**, 28-36, 2000.

The absorption spectrum of HDO in the 16300-16670 cm⁻¹ and 18000-18350 cm⁻¹ spectral regions, A. Campargue, E. Bertseva, and O. Naumenko, *J. Mol. Spectrosc.* **204**, 94-105, 2000.

Case 5: Ozone O₃ (1)

The temperature dependence (203-293 K) of the absorption cross-sections of O₃ in the 230–850 nm region measured by Fourier-transform spectroscopy, S. Voigt, J. Orphal, K. Bogumil, and J. P. Burrows, *J. Photochem. Photobiol. A* **143, 1–9, 2001.**

An accurate wavelength calibration for the Ozone absorption cross-Section in the near-UV spectral region, and its effect on the retrieval of BrO from measurements of zenith-scattered sunlight, N. Mohammed-Tahrin, A. M. South, D. A. Newnham, and R. L. Jones, *J. Geophys. Res. D* **106, 9897-9907, 2001.**

A critical review of the absorption cross-sections of O₃ and NO₂ in the 240-790 nm region. Part I: Ozone, J. Orphal, *Report for the GOME Science Advisory Group*, ESA Special Publication, 124 pp., ESA Earth Sciences Division, ESTEC, Noordwijk, 2001.

Case 5: Ozone O₃ (2)

Temperature-dependent absorption cross-sections of O₃

511

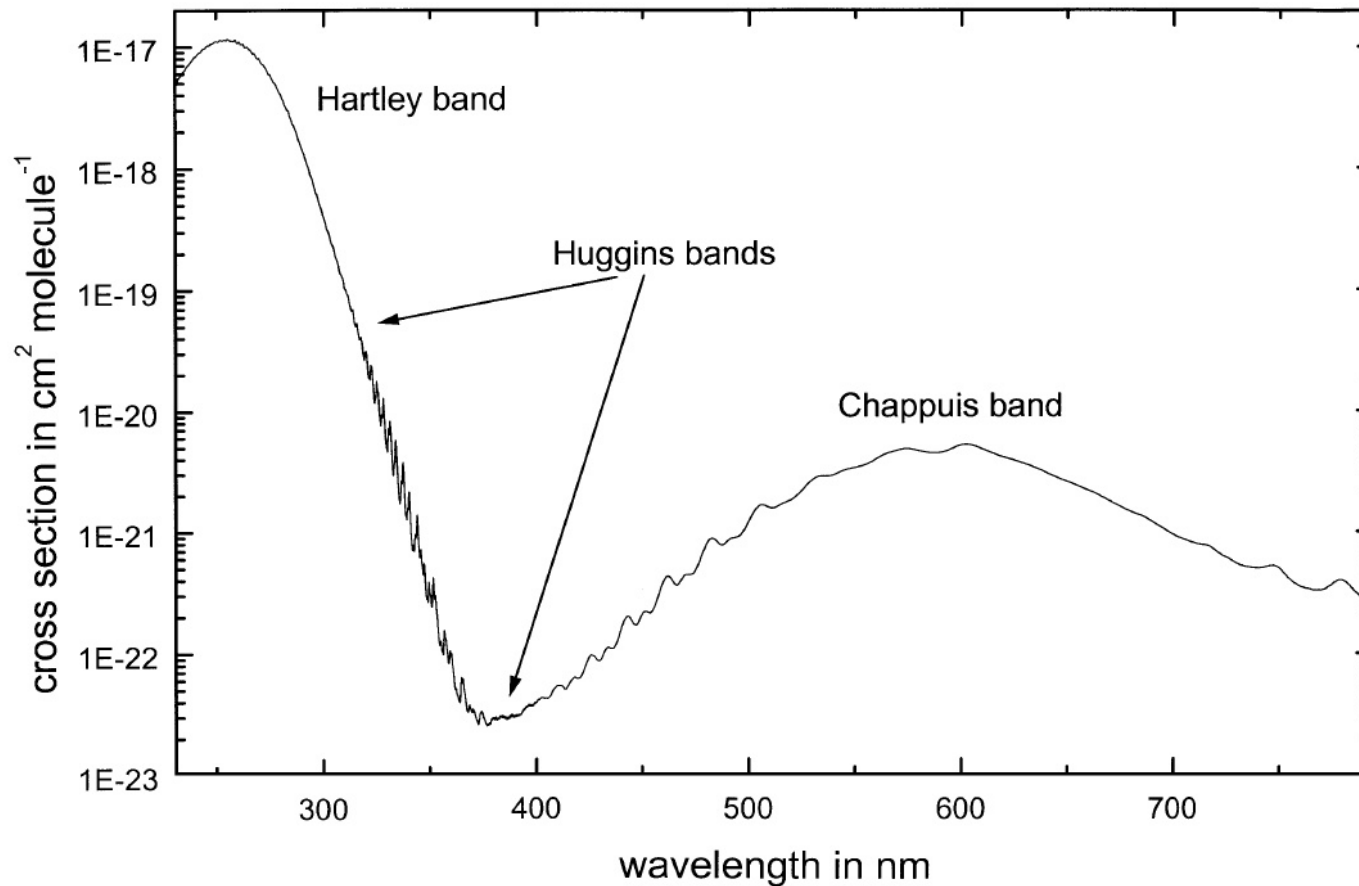


Fig. 1. The O₃ absorption cross section spectrum at 293 K as measured with the GOME FM spectrometer. The spectral resolution is about 0.2 nm at wavelengths below and about 0.3 nm above 400 nm. The different bands discussed in the text are indicated. Note the logarithmic y-scale, and the complete coverage of the 231–794 nm range.

Source: J. P. Burrows et al., *J. Quant. Spectrosc. Rad. Transf.* 61, 509-517, 1999.

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Case 5: Ozone O₃ (3)

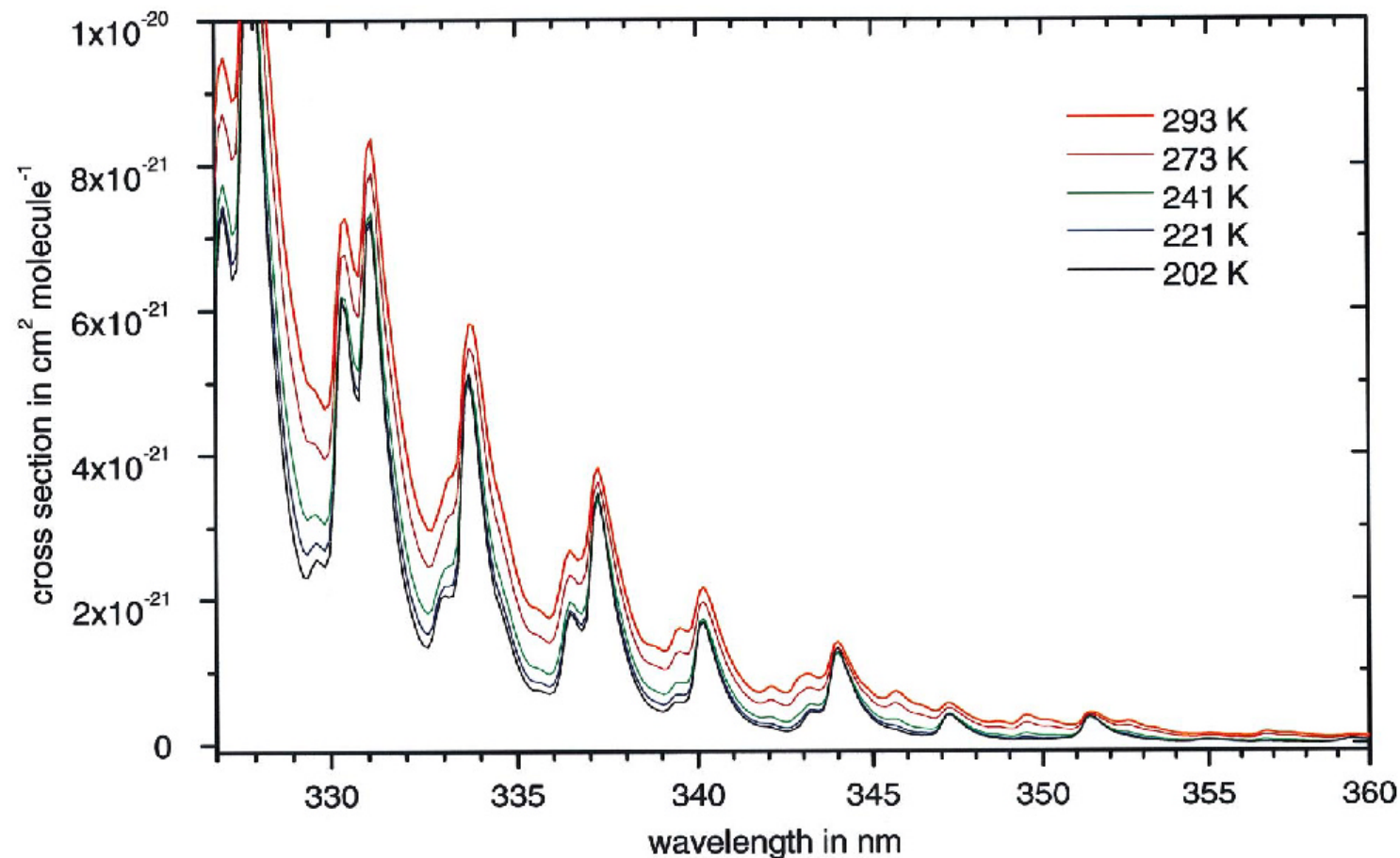
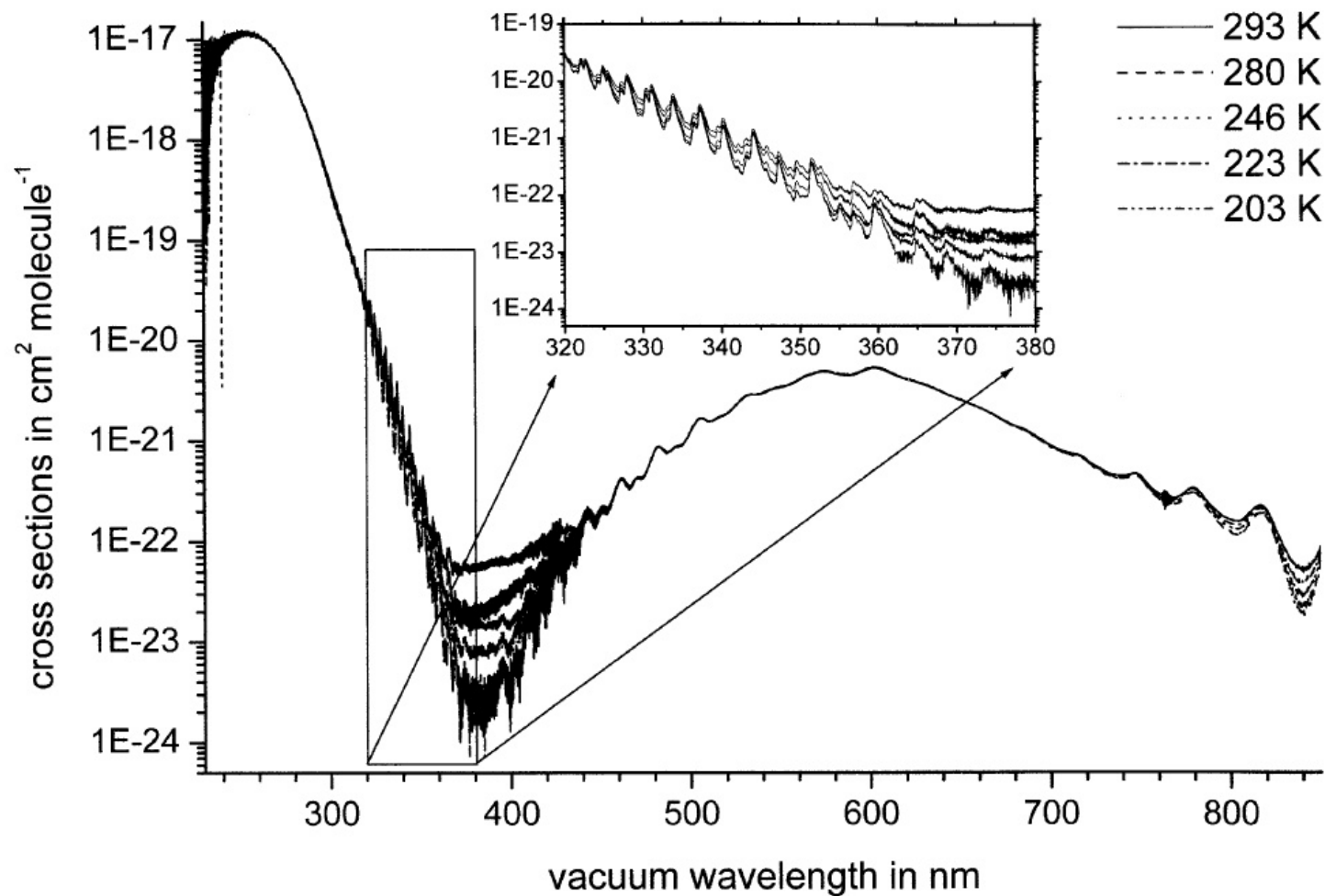


Fig. 5. The absorption cross sections of O₃ in the Huggins bands, showing a strong temperature dependence. The differential absorption cross sections increase in a non-linear way with temperature, probably due to the presence of hot bands at higher temperatures and to congestion by rotational depopulation of the lower states. Several hot bands appear at wavelengths above 340 nm.

Source: J. P. Burrows et al., *J. Quant. Spectrosc. Rad. Transf.* 61, 509-517, 1999.

Case 5: Ozone O₃ (4)

S. Voigt et al./Journal of Photochemistry and Photobiology A: Chemistry 143 (2001) 1–9

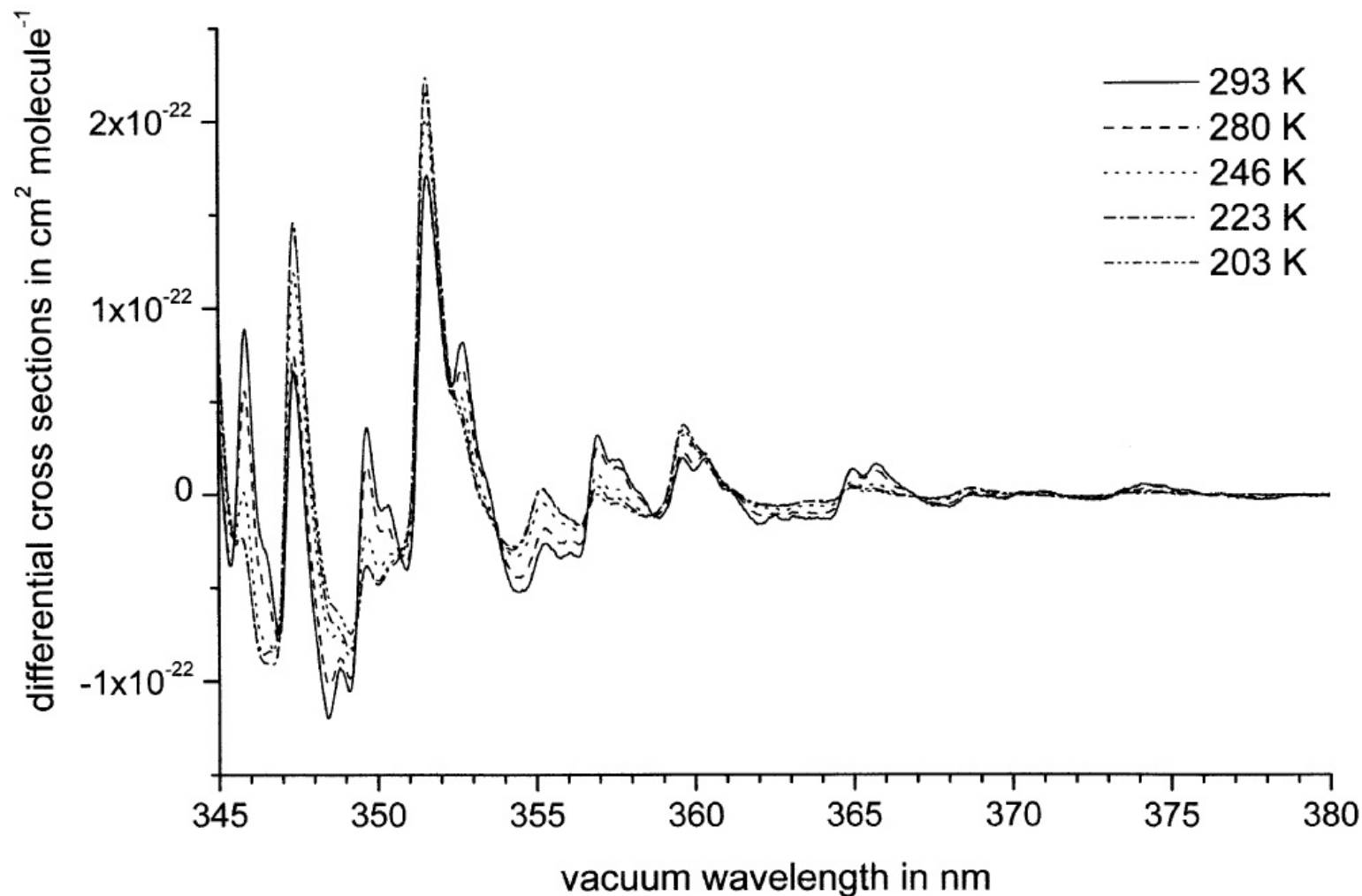


Source: S. Voigt et al., J. Photochem. Photobiol. A 143, 1-9, 2001.

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Case 5: Ozone O₃ (5)

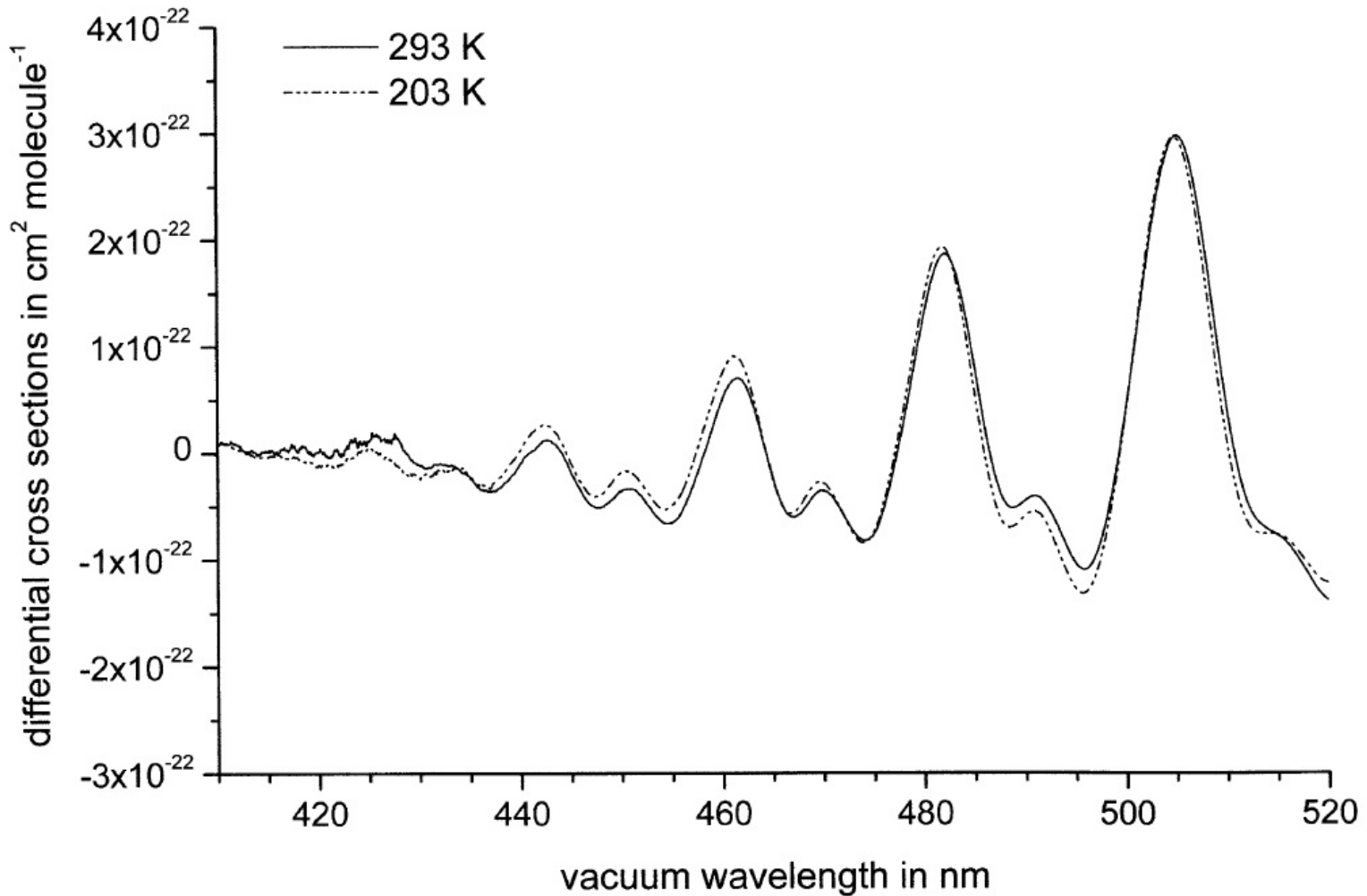
S. Voigt et al./Journal of Photochemistry and Photobiology A: Chemistry 143 (2001) 1–9



Source: S. Voigt et al., J. Photochem. Photobiol. A 143, 1-9, 2001.

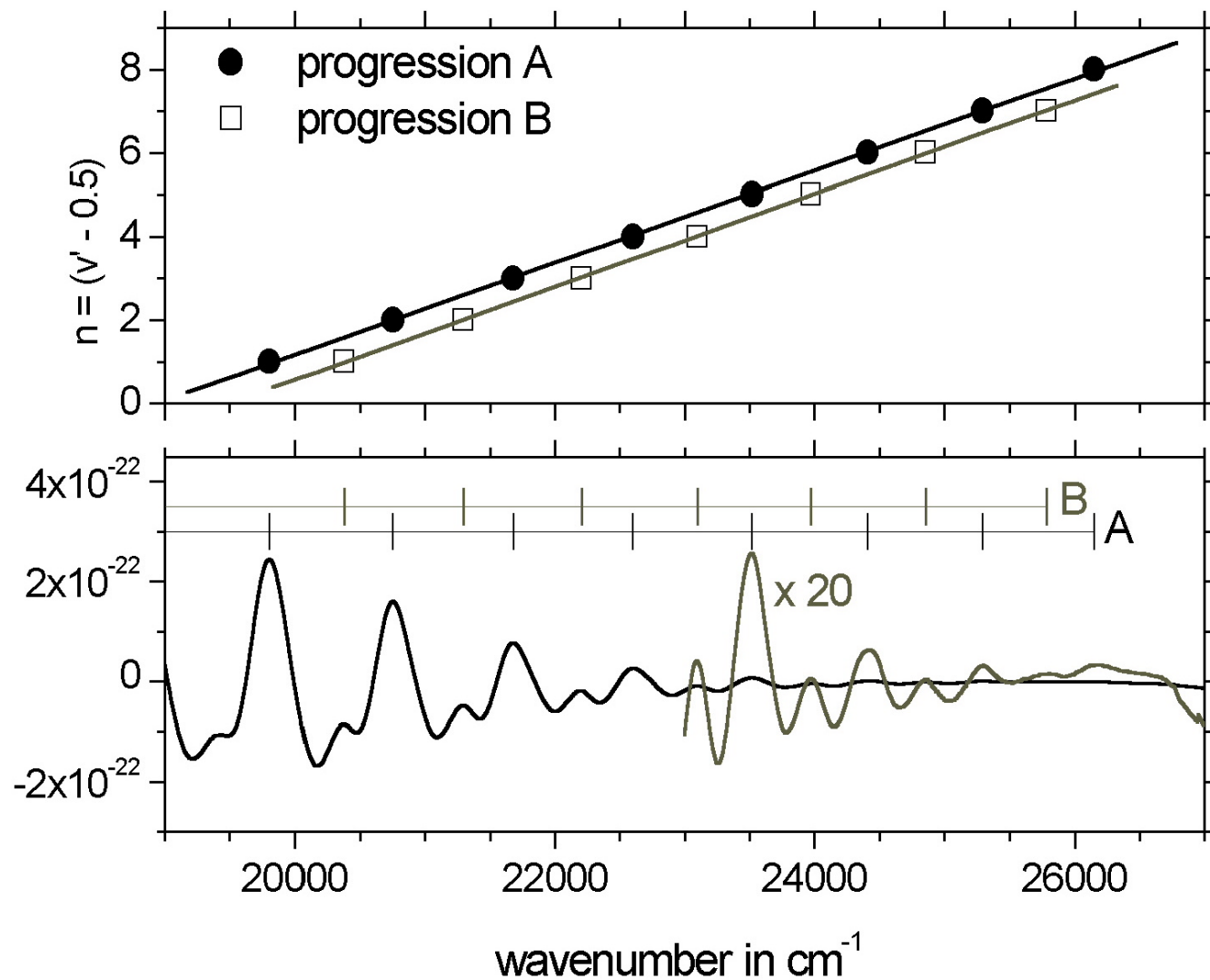
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Case 5: Ozone O₃ (6)



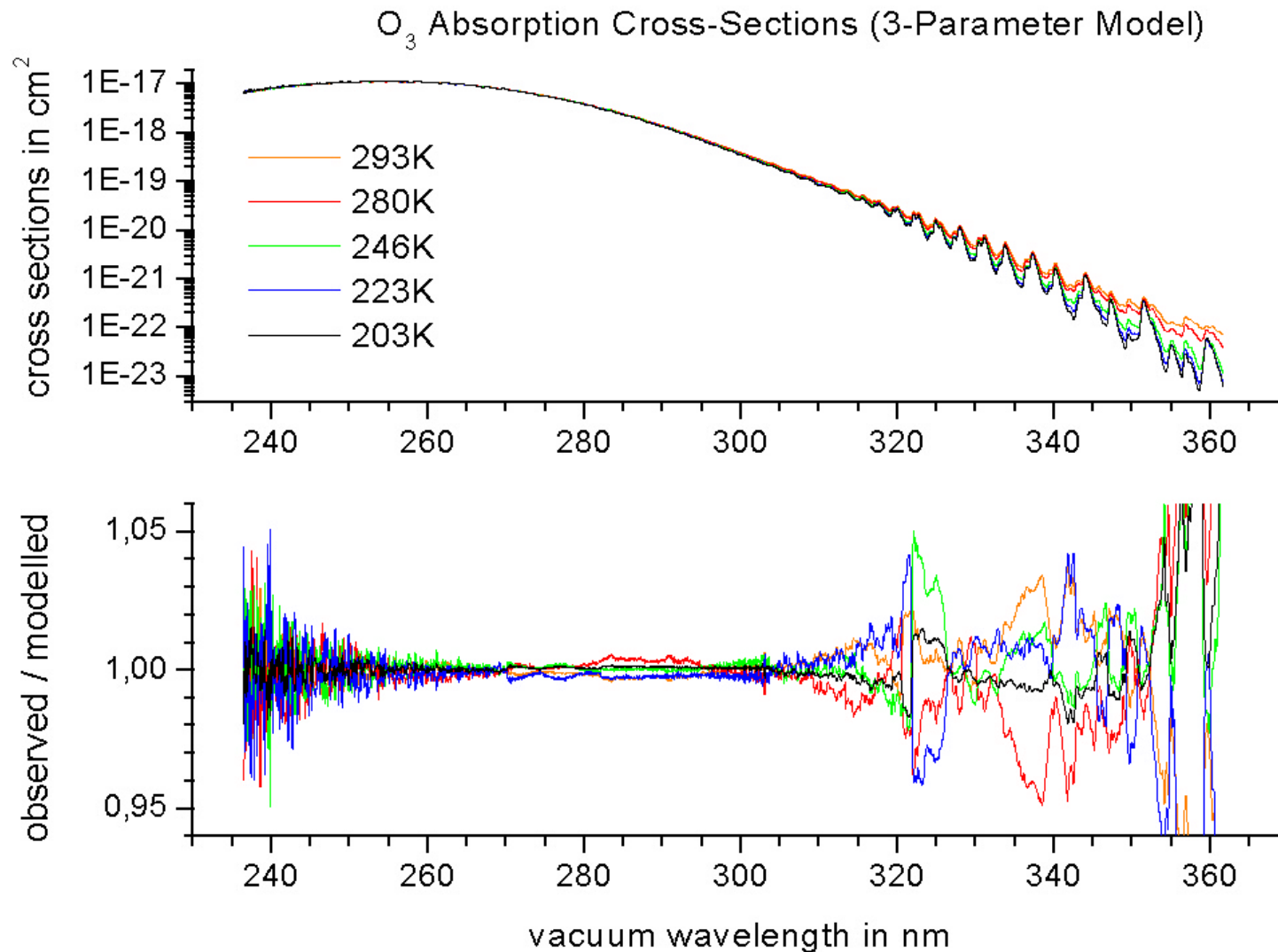
Source: S. Voigt et al., J. Photochem. Photobiol. A 143, 1-9, 2001.

Case 5: Ozone O_3 (6a)



Source: K. Bogumil et al., Chem. Phys. Lett., in press.

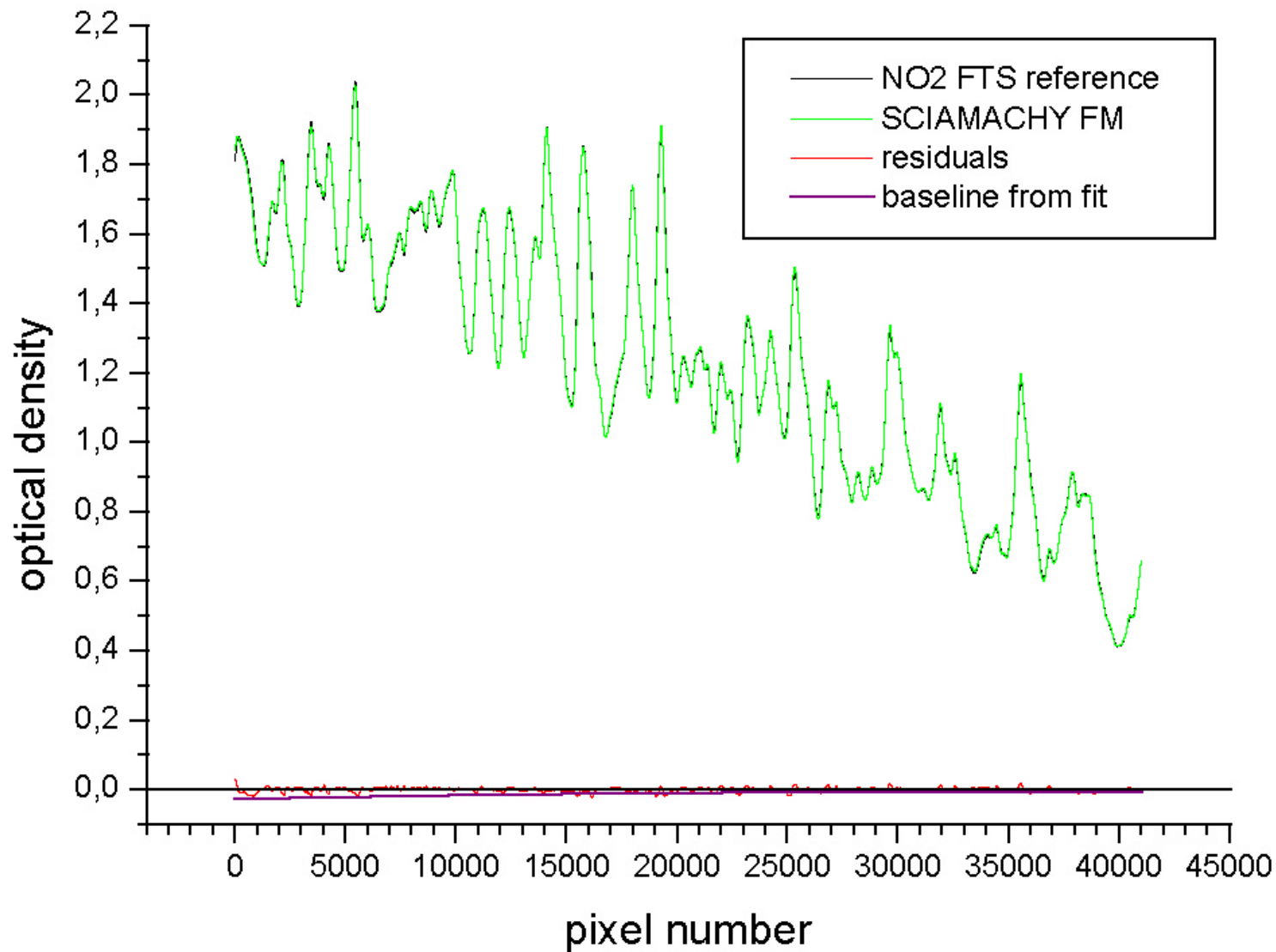
Case 5: Ozone O₃ (7)



Source: S. Voigt et al., J. Photochem. Photobiol. A 143, 1-9, 2001.

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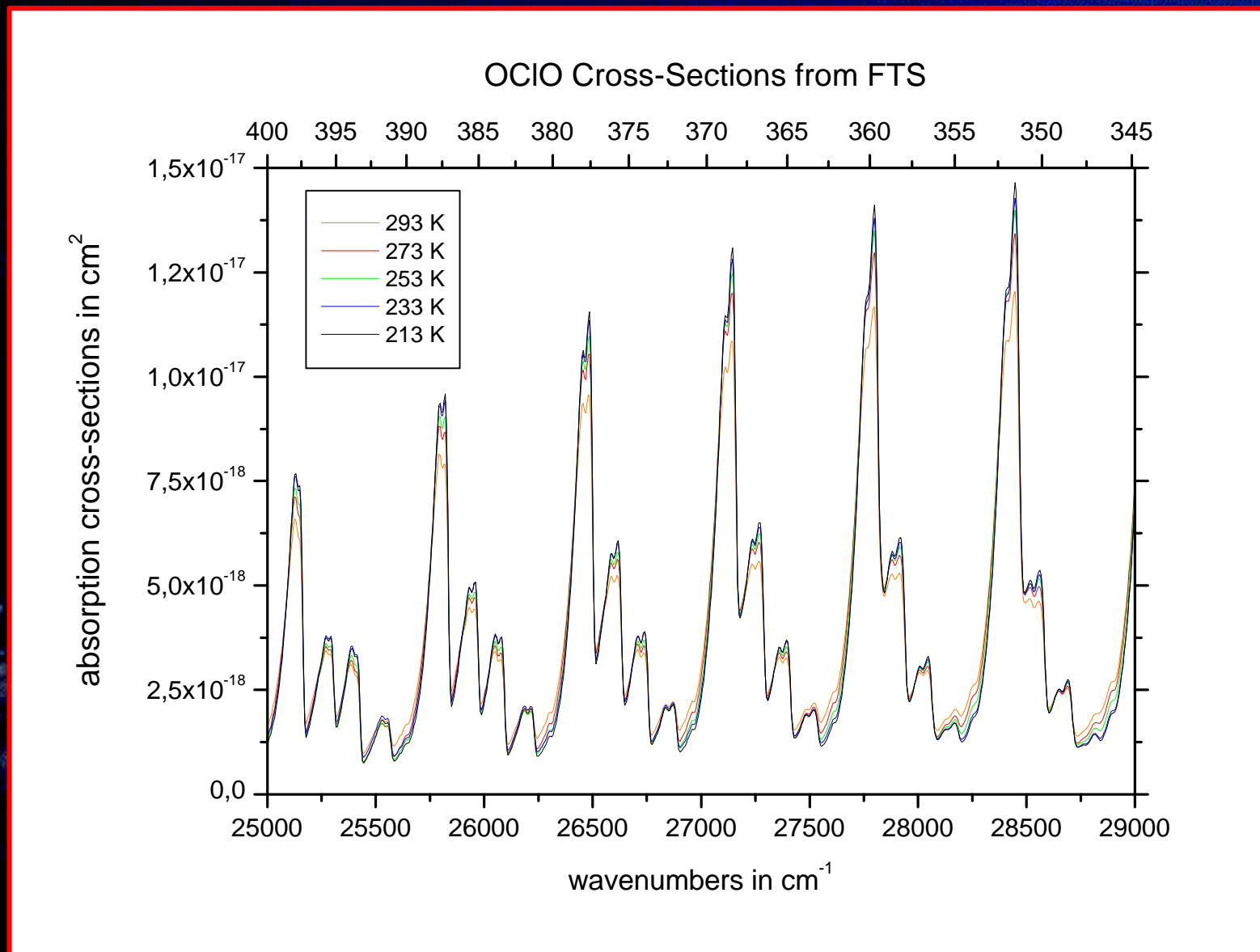
Case 6: Nitrogen dioxide NO₂



Source: J. Orphal, Critical Review Part 2. NO₂, ESA-ESTEC, 2001.

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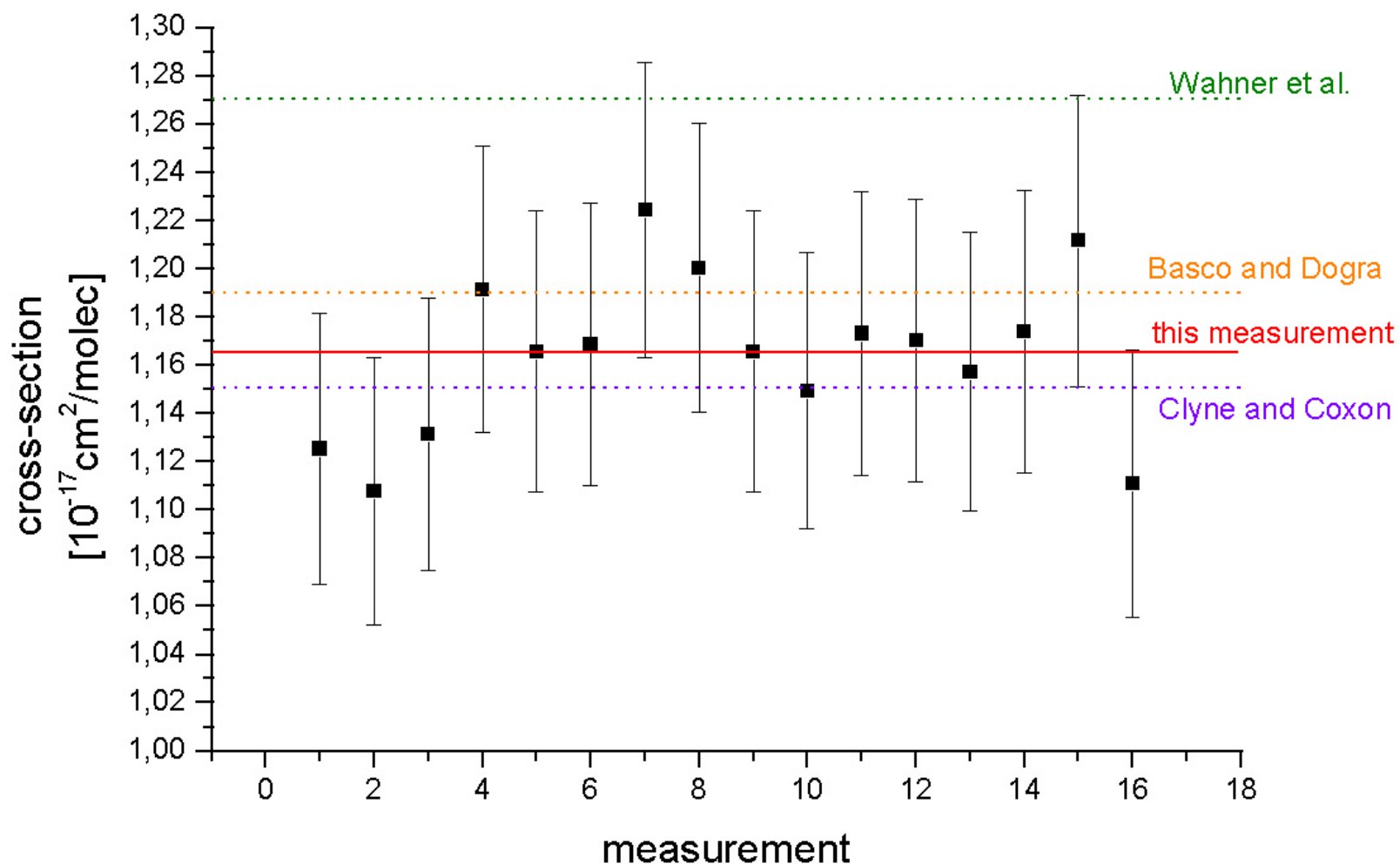
Case 7: Chlorine dioxide OClO (1)



Source: H. Kromminga, et al., *J. Photochem. Photophys. A*, submitted, 2001.

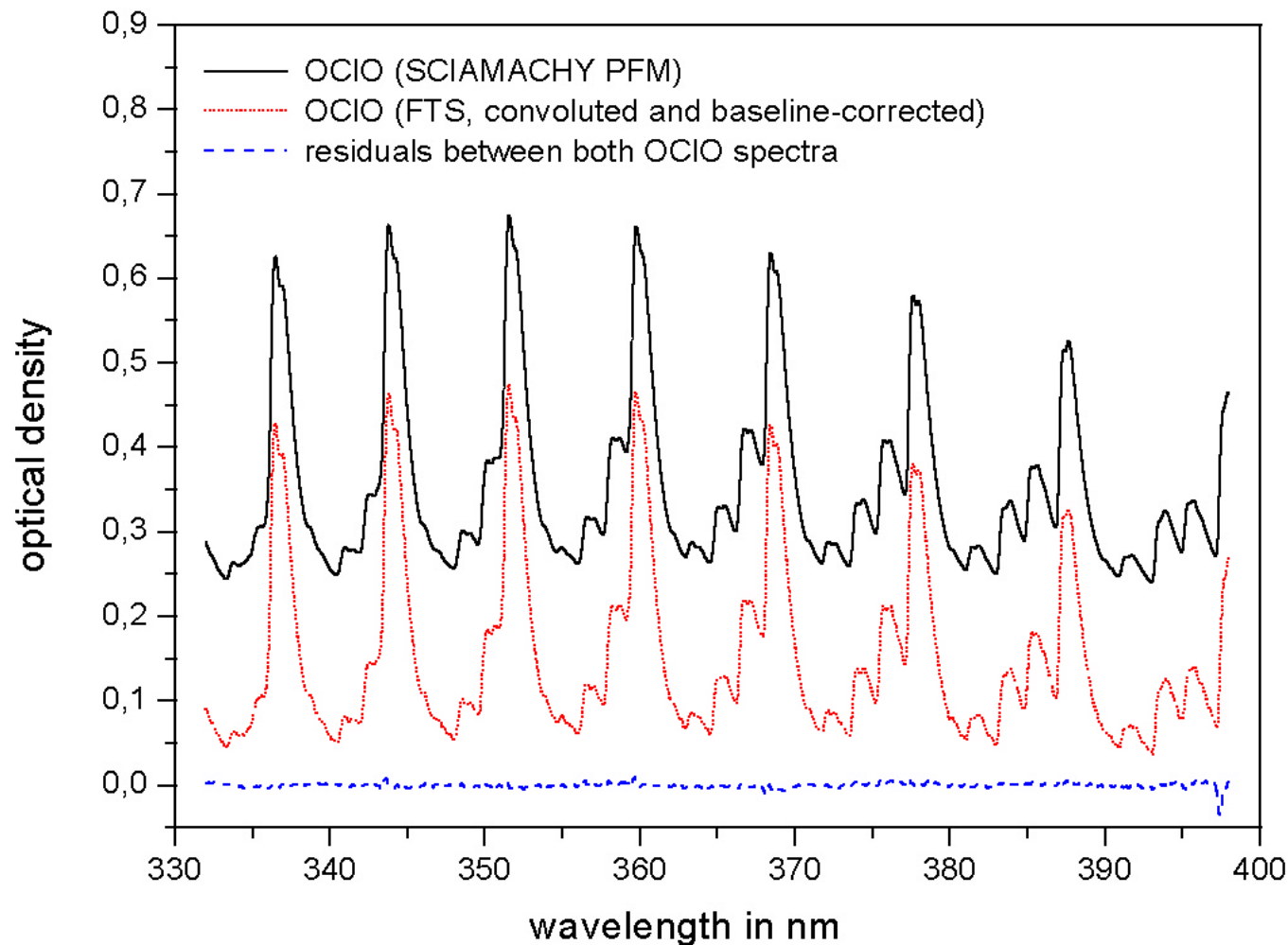
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Case 7: Chlorine dioxide OClO (2)



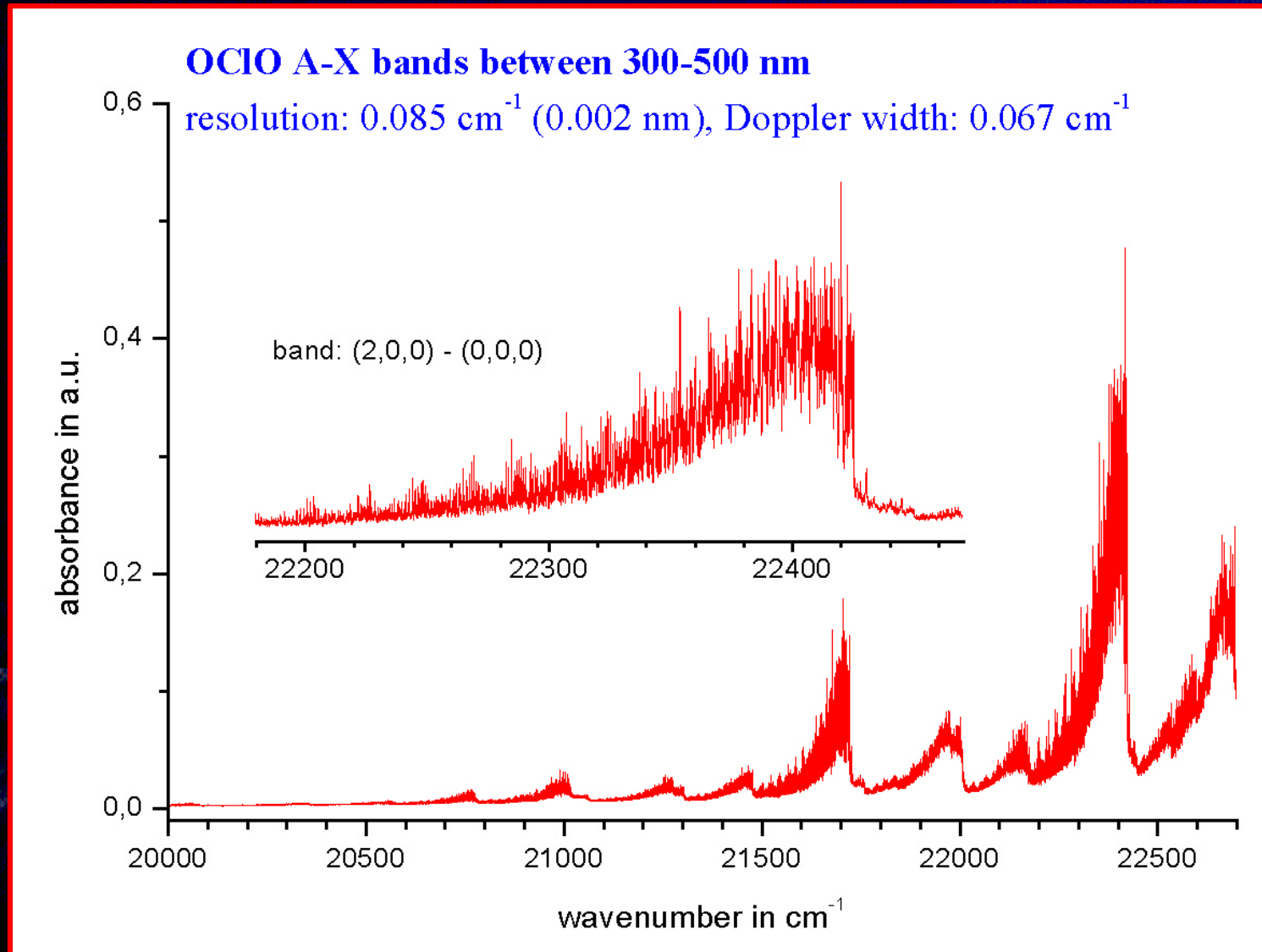
Source: H. Kromminga, et al., *J. Photochem. Photophys. A*, submitted, 2001.

Case 7: Chlorine dioxide OCIO (3)



Source: H. Kromminga, et al., J. Photochem. Photophys. A, submitted, 2001.

Case 7: Chlorine dioxide OClO (4)



Source: J. Orphal, unpublished data, 1997.

Case 8: Bromine monoxide BrO (1)

Cavity ring-down spectroscopy of the $A^2P_{3/2} - X^2P_{3/2}$ transition of BrO, S. M. Newman, W. H. Howie, I. C. Lane, M. R. Upson, and A. J. Orr-Ewing, *Chem. Phys. Lett.* **285**, 346-351, 1998.

Fourier transform ultraviolet spectroscopy of the $A^2P_{3/2} \rightarrow X^2P_{3/2}$ transition of BrO, D. M. Wilmouth, T. F. Hanisco, N. M. Donahue, and J. G. Anderson,, *J. Phys. Chem. A*. **103**, 8935-8945, 1999.

Time-windowing Fourier transform absorption spectroscopy for flash photolysis investigations, O. C. Fleischmann, J. Orphal, and J. P. Burrows, *manuscript in preparation*, 2001.

Case 8: Bromine monoxide BrO (2)

A $^2\Pi_{3/2} \leftarrow X\ ^2\Pi_{3/2}$ Transition of BrO

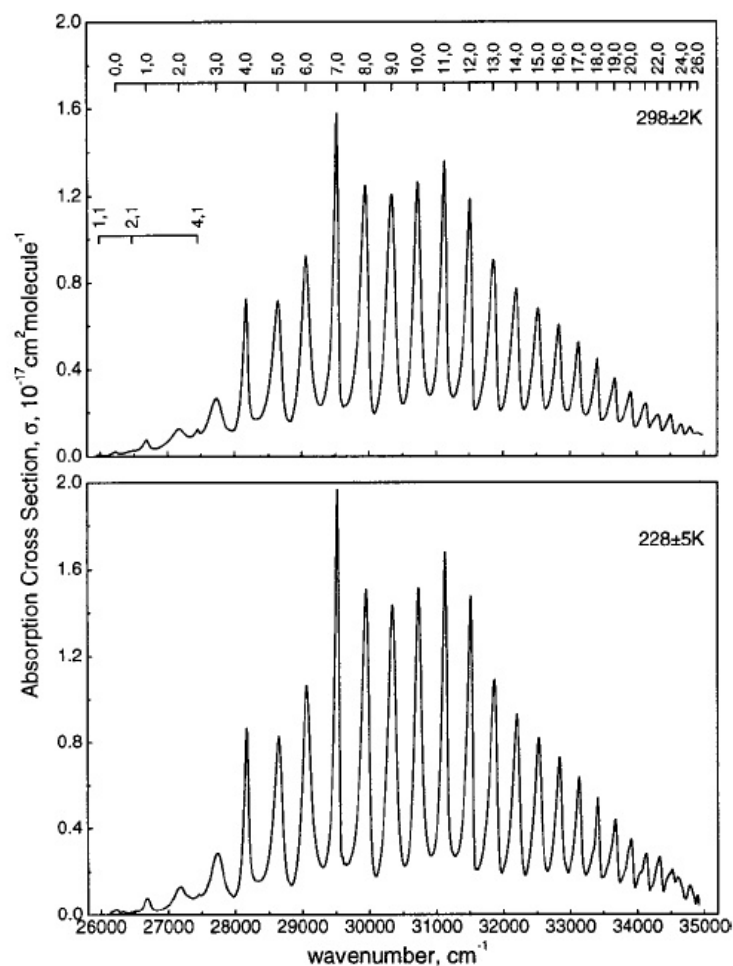
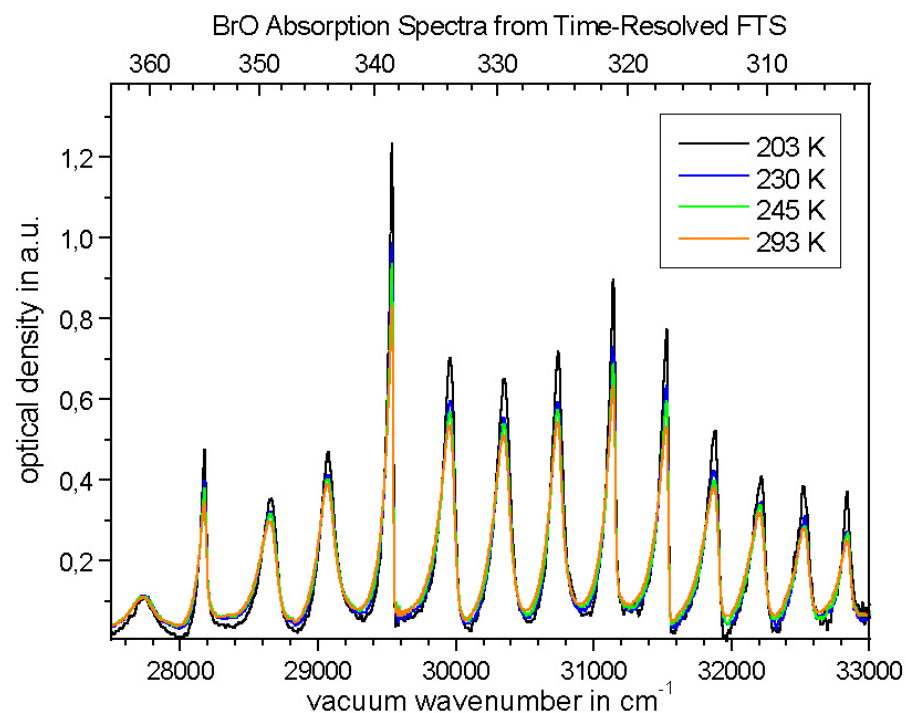


Figure 2. UV absorption spectra of the A $^2\Pi_{3/2} \leftarrow X\ ^2\Pi_{3/2}$ transition of BrO at $298 \pm 2 \text{ K}$ and $228 \pm 5 \text{ K}$. Spectra were acquired at 10 cm^{-1} resolution with no apodization and are displayed here degraded to 35 cm^{-1} resolution with triangular apodization. Cross sections are normalized to the 7,0 band cross section. The vibrational transitions (v', v'') are listed at the top of the 298 K spectrum.



Sources: *D. Wilmouth et al., 1999;*
O. C. Fleischmann et al., 2001.

Case 9: Bromine monoxide BrO (3)

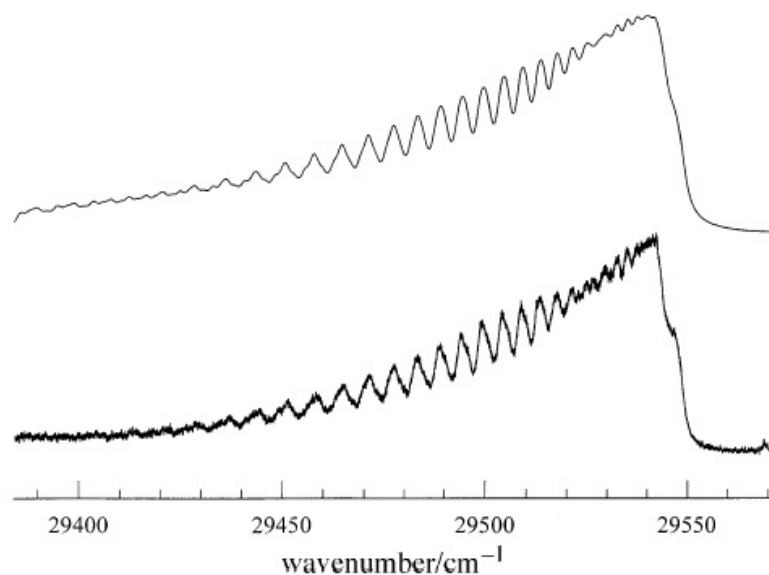


Fig. 11 CRD spectrum of the BrO $A^2\Pi_{3/2}-X^2\Pi_{3/2}$ (7, 0) band, together with a spectral simulation (above). The simulation includes both isotopes of Br in their appropriate natural abundances and a rotational linewidth of 3.2 cm^{-1} to account for lifetime broadening. The tail of the band corresponds to transitions between levels with rotational quantum numbers of $N \approx 30-40$.

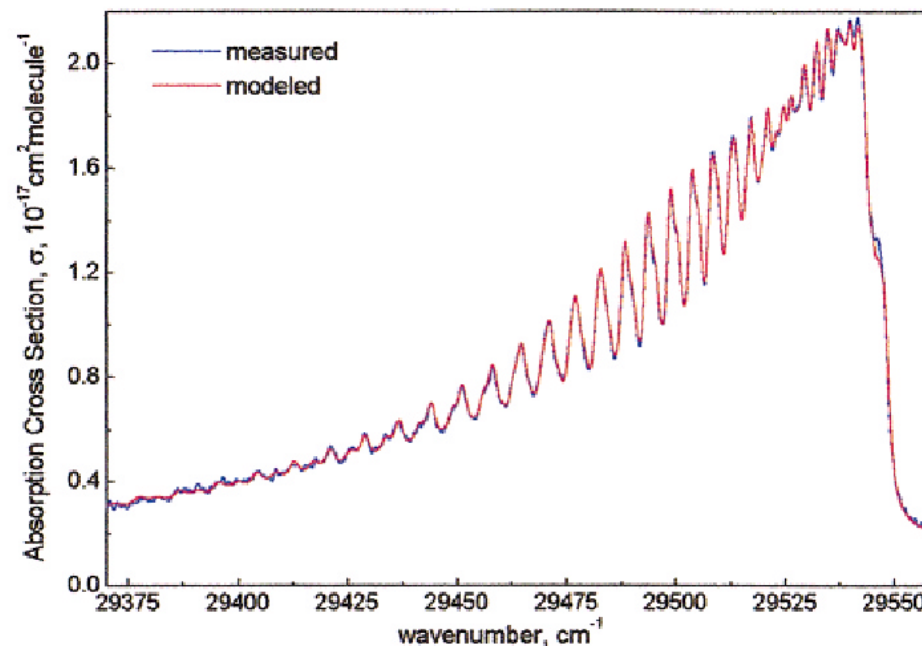
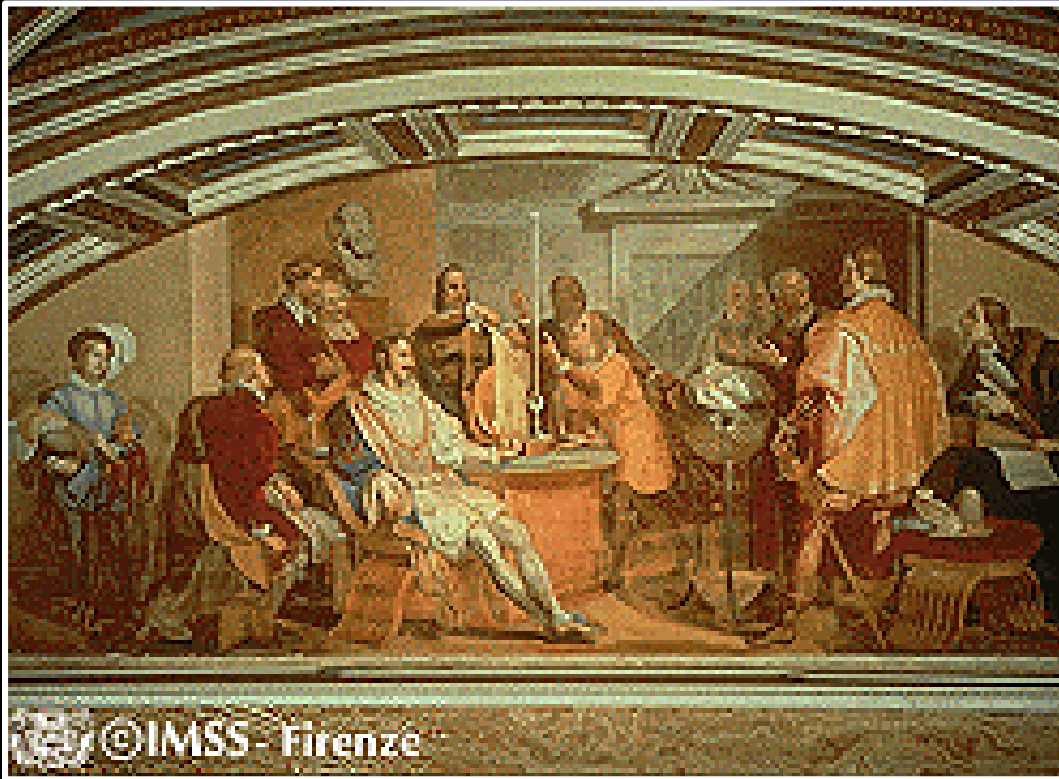


Figure 4. 1.0 cm^{-1} resolution UV absorption spectrum of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ 7,0 band of BrO at $298 \pm 2\text{ K}$. The modeled 7,0 spectrum, shown overlaying the measured spectrum, was produced using the method described in the text.

Sources: S. Newman et al., 1998; D. Wilmouth et al., 1999.

What I did not speak about:

- CH_2O , SO_2 , NO_3 , HONO, IO, OIO, OH, NO, OBrO
- organic molecules (glyoxale, benzene, toluene, phenole, para-cresole, para-xylol, ...)
- the difficulties to model electronic transitions
- the difficulties to compare laboratory data
- what I think what experimental and theoretical spectroscopy could achieve in the next decade
- ...



But :
The users need standards.

The liquid in glass thermometer was developed in the 1630s, but a universal standard of temperature remained elusive. Each scientist had his own scale divisions, often based on different reference points.

*It is impossible for us accurately to convert their measurements to our temperature scale, **and** at the time it was impossible to compare temperatures in different places.*

In the early eighteenth century, universal temperature scales based on several fiduciary points (e.g. a mixture of ice and brine, a mixture of ice and water, body temperature, the boiling point of water) were developed by Daniel Gabriel Fahrenheit (1686-1736), Anders Celsius (1701-1744), and René-Antoine Ferchault de Réaumur (1683-1757).

*Of these, the first two are still in use, and the system of Celsius (extended to become an absolute scale in the nineteenth century) **has become** the standard temperature scale more than 200 years later. (source: W. E. Knowles Middleton, *The History of the Thermometer and its Use in Meteorology* (Baltimore: Johns Hopkins University Press, 1966).)*

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